CELLULOSE RESEARCH

Symposium II – 1958

COUNCIL OF SCIENTIFIC &
INDUSTRIAL RESEARCH, NEW DELHI

Cellulose Research

Symposium II — 1958

Cellulose constitutes the basic material for some of India's biggest industries — cotton textiles, jute, paper and rayon — and for this reason, the results of investigations directed to the understanding of its structure and properties and its utilization in industry are of continuing interest to research workers, industrialists, and users of cellulose products alike. This publication presents the papers discussed at the symposium, the second in the series, organized by the C.S.I.R. Cellulose Research Committee under the following sections:

Structure and Physical Properties of Cellulose

Chemistry and Technology of Cellulose

Chemical Pulp in Relation to Rayon Industry

Mechanical Pulp with special reference to the Paper Industry

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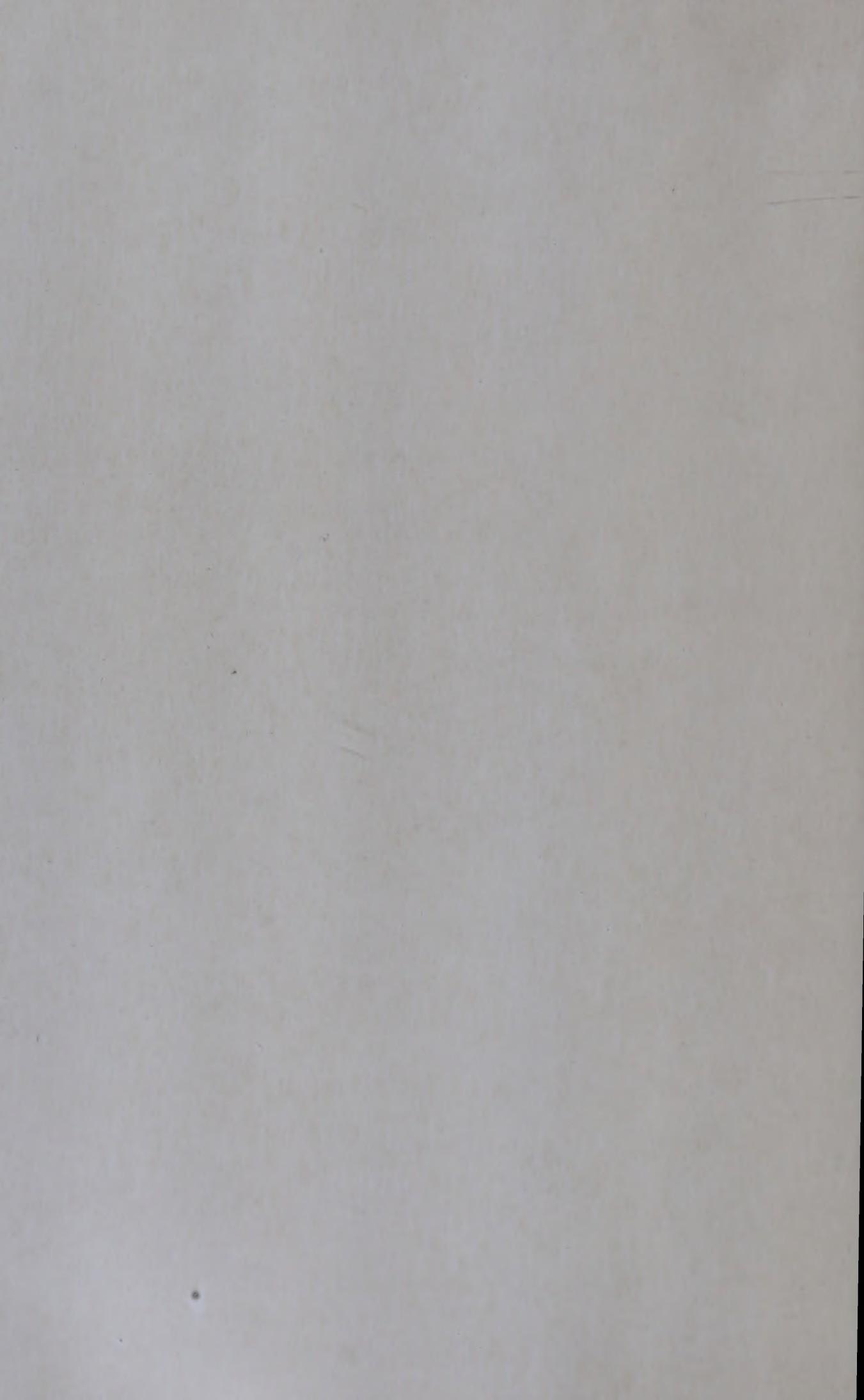
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NEW DELHI

PREFACE

Eighteen papers, presented at the First Cellulose Symposium held at Ahmedabad in February 1957, dealt with the structure and mechanical properties of cellulose, chemistry of cellulose, pulp and paper, rayon and jute. The plan followed for the Second Symposium held in February 1958 at Dehra Dun was somewhat wider in scope, the general topics brought before the meetings being structure and physical properties of cellulose, chemistry and chemical technology of cellulose, chemical pulp in relation to the rayon industry and mechanical pulp with special reference to paper industry. These subjects were covered by twenty-seven papers read and discussed in four sessions. Thus in the number and variety of material presented as also in the number of institutions contributing papers and delegating their representatives to the meetings, the Second Symposium showed a noteworthy advance. The interest in the meetings was keen and a number of research schemes in progress under the *Cellulose Research Committee*, as well as those freshly proposed to the same body, were fully discussed.

Dr. R. V. Bhat, Officer-in-charge (till recently) of the Cellulose & Paper Branch of the *Forest Research Institute*, Dehra Dun, organized the meetings. The compilation and editing of papers were undertaken by me, and this work I have done with great pleasure, at the request of Dr. Vikram Sarabhai, Chairman of the *Cellulose Research Committee*.

Ahmedabad
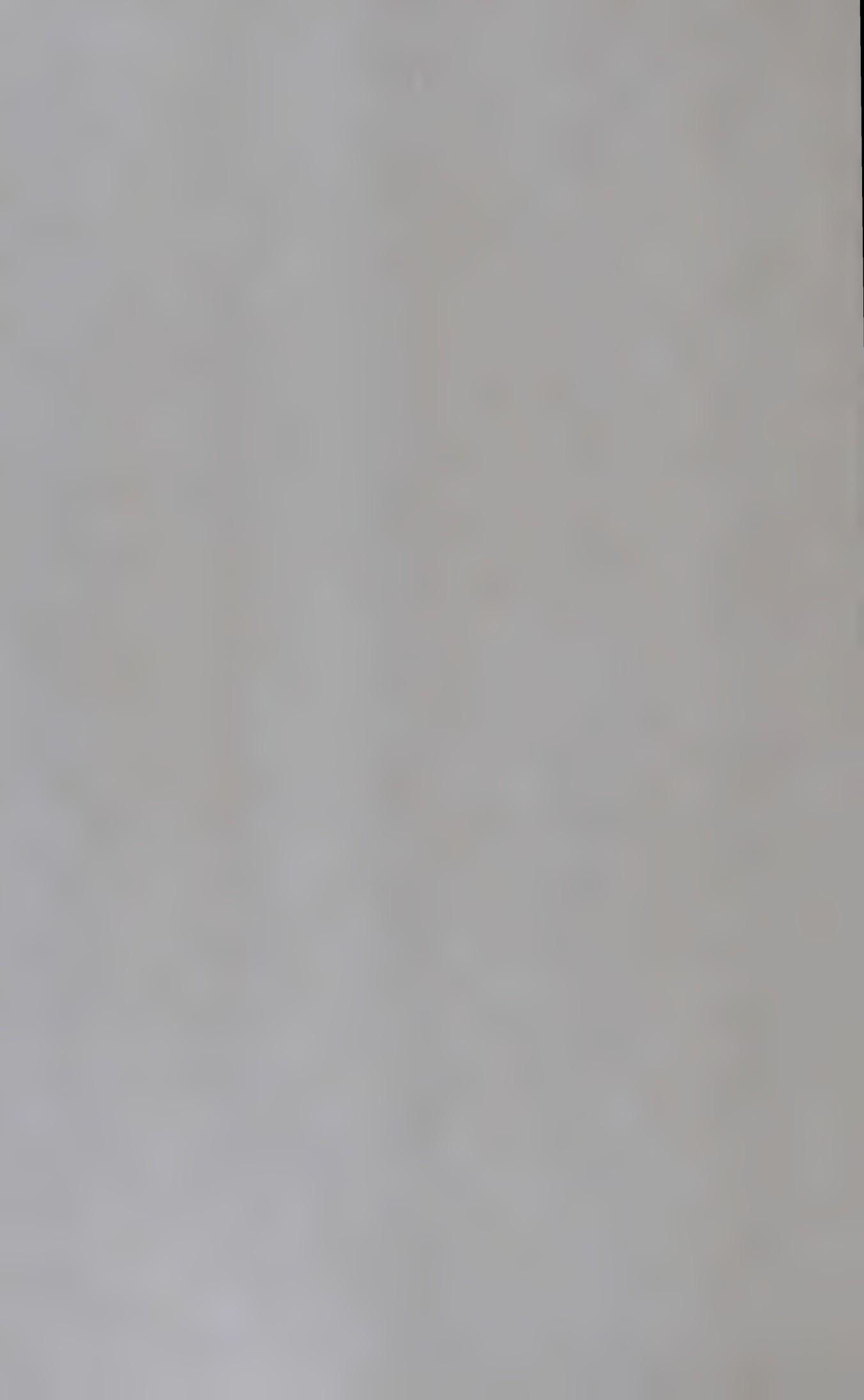July 20, 1959   B. K. VAIDYA

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Microbiological Studies on Fibre Degradation

Welcome Speech

R. N. DATTA

President; Forest Research Institute and Colleges, Dehra Dun

It gives me great pleasure to accord a most hearty welcome to you all to the *Forest Research Institute* to hold this Symposium.

This Institute was established in the year 1906. It has a Cellulose & Paper Branch which has been in existence since the establishment of the Institute. This Branch, I am glad to say, has already contributed a great deal to the development of the Indian paper industry from indigenous raw material obtainable in our forests and wastelands and as byproducts of agriculture. We have recently started research on the preparation of high alpha-cellulose pulp for viscose pulp rayon and nitrocellulose from indigenous cellulosic materials and encouraging results have been obtained.

The earliest attempts to manufacture paper in this country can be traced back to 1870. In due course a few paper mills came up and, before the last war, there were only 9, the annual production of which was only about 48,500 tons. Although the war curtailed supplies from foreign sources, the protection given by the government to the industry provided the incentive for expansion. The protection was, however, withdrawn in 1947. There were 17 mills with a capacity of 1,36,000 tons in 1951. The gap between our requirements and indigenous production still remained quite wide and we had to import about 1,76,000 tons of paper, boards and newsprint in 1951-52.

The spread of education and the needs of our expanding industries have necessitated a considerable expansion of the paper and pulp industry and, to meet these needs, the production of paper and boards has increased to about 2 lakh tons and some newsprint has also been produced under the First Five-Year Plan. As you know, further expansion is envisaged in the Second Five-Year Plan under which the target for paper and board is fixed at 3,50,000 tons, for newsprint at 60,000 tons and for rayon grade pulp at 30,000 tons.

of cellulose research. It would be unfair to expect the reviewers to be able to cover completely all the aspects and I have, therefore, left it open to them to pick and choose.

If any of the research workers here feels that any new development has not been touched upon by the reviewers, I would like him to express his views.

One of the review talks was to be given by Dr. H. Wakeham, Director of the *Ahmedabad Textile Industry's Research Association*, Ahmedabad, on *Progress in Physics and Physical Chemistry of Cellulose*, 1957. He had kindly agreed to give the talk, but he could not be present here as he has been advised by his doctors not to undertake the trip. I, therefore, made a hurried approach to Dr. Radhakrishnan who has kindly agreed to make his own presentation of this talk and I am very grateful to him for undertaking this job.

We have the privilege of having the following gentlemen as chairmen of the various sessions: Dr. M. K. Sen—Session I: *Structure and Physical Properties of Cellulose*; Dr. K. Venkataraman—Session II: *Chemistry and Chemical Technology of Cellulose*; Dr. H. Parekh—Session III: *Chemical Pulp in relation to Rayon Industry*; Dr. R. V. Bhat—Session IV: *Mechanical Pulp with special reference to the Paper Industry*.

I would ask these gentlemen to give us the advantage of their experience and guide the proceedings. As far as other speakers are concerned, we expect a presentation of their contributions.

I am grateful that we have been provided a very generous organizational help from this Institute, its President and the organizing Secretary, Dr. Bhat. Though Dr. Bhat has been occupied with his own duties, he has taken the trouble to shoulder this responsibility and we are deeply grateful to him.

I would like to mention in this context that the CSIR has brought out a special volume of the papers which were presented last year to the Symposium. We hope to bring out a similar publication this time also.

Structure and Mechanical Properties of Cellulose

T. RADHAKRISHNAN

Ahmedabad Textile Industry's Research Association, Ahmedabad

Most of the systematic progress in cellulose physics can be brought under the intimately related study of fine structure and mechanical properties.

FINE STRUCTURE

The fine structure of textile fibres covers a dimensional range from Angstroms to microns. The appropriate physical tools for revealing their structure are light and electron microscopy, X-ray diffraction, spectroscopy and various techniques employing polarized radiation. These tools help in gaining a knowledge of: (*i*) the internal appearance of fibres, (*ii*) the degree of short-range lateral order or crystallinity, (*iii*) the degree of longitudinal order or orientation and (*iv*) the degree of long-range order, or micellar structure.

Internal appearance of fibres

In order to look inside a fibre, one uses electron microscopy and some advanced techniques in light microscopy as well. For getting a skin-deep look, the chief problem is to obtain a replica of the fibre surface which is robust enough to withstand an electron beam. Replicas are obtained by (*i*) lightly pressing the fibre on a medium of the right plasticity, e.g. drying parlodion solution on a glass microscope slide, (*ii*) withdrawing the fibre, (*iii*) peeling off the hardened replica, and (*iv*) strengthening and shadow-casting it in the conventional manner. The success of the process depends on skill, experience and scrupulous attention to detail. Three variants of the replica making process have been described[1-3]. Two papers[4,5] describe the technique of making aluminium replicas which are suitable for light microscopy. These latter can be peeled off the fibre and flattened out, so that the depth of field problems in the light microscope are minimized.

The outstanding result of the electron microscopy of surface replicas has been the discovery[3] of a ridge groove system which spirals at an angle of 20° to 30° to the fibre axis along the outside of the primary wall of native cotton fibres.   The ridges and grooves are about $\frac{1}{2}\mu$ wide and 10μ long and may occasionally reverse in direction every 100μ or so.   The similarity of the phenomenon to the spiral structure of fibrils lying below the primary wall and to the structural reversals found in cotton is evident.   It has been found that the spiral ridge groove system disappears when the fibre is subjected to treatments which may damage the primary wall, such as abrasion and scouring.   Moreover, the appearance of the surface is markedly altered by the presence of additives, such as starch, colloidal silica, carboxymethyl cellulose and some acrylic polymer resins.   Fig. 1 shows the electron micrograph of cotton surface.

Kassenbeck[6] has described a technique (double cutting technique) for making ultra-thin fibre cross-sections (100 to 300 A).   Sections of viscose rayon prepared by this technique were examined in the electron microscope. The differences in packing density between the skin and the core were readily apparent and further, it appeared as though the coagulation of the skin was periodically stratified.

The easiest of fibre studies using the electron microscope is the study of fibrils.   A few papers[7,8] have described the best conditions for ultrasonic

Fig. 1—Electron micrograph of the surface of cotton fibre

TABLE 1—PERCENTAGE VALUES OF NON-CRYSTALLINITY AND ACCESSIBILITY OF CELLULOSIC FIBRES

	NON-CRYSTALLINE			ACCESSIBLE		
	Hydrolysis	X-Ray	Density	D_2O	Formy-lation	Thallous ethylate
Cotton	6 - 8	30 - 31	40	44	12.5	0.4
Wood pulp	9 - 11	30	47	55	..	..
Mercerized cotton	11 - 14	..	60	..	20	3.3 - 27
Fortisan	..	51	..	..	..	..
Fibre G	..	47	54	67	..	..
Textile rayon	..	60 - 63	75	68	39	..
High tenacity rayon	27 - 31	60 - 61	..	86	..	..

disintegration of fibres into fibrils. A controversial series of papers on fibrillar structure in diluted solutions of cuprammonium and viscose has also been published in which claims that these solutions contain hitherto unsuspected structural forms of cellulose and that evaporated nitrocellulose solutions contain accummulation of low molecular cellulose chains and short-chain hemicelluloses have been made[9]. This work, which is based on electron microscopy as well as on small-angle X-ray scattering, has been criticized by authorities like Frey-Wyssling[10].

Advanced techniques in light microscopy, such as the use of interference and phase contrast microscopy, have recently found increasing application to fibres[11]. A paper on the use of the interference microscope in fibre research has appeared in 1957[12]. This type of microscope permits the observation and measurement of minute difference in refractive index within the object field, threby enabling a vivid differentiation of details, like cell wall and lumen, primary and secondary wall, skin and core. It is an easier tool for the measurement of refractive index than the Becke line method and, moreover, local variations of refractive index can be measured, whereas by the other methods, on the refractive index at the fibre surface or the average value for the whole fibre can be measured.

Crystallinity

Crystallinity is a term which has had various meanings to the physicist and chemist. It has been found imperative to differentiate between crystallinity and accessibility and in the case of accessibility, to specify the method by which it is determined. An examination of Table 1 will make this point clear.

Crystallinity is probably best defined as the fraction of cellulose which gives a crystalline or sharp X-ray diffraction. Even this definition lacks rigour, because one cannot distinguish between two types of diffuseness in X-ray

diffraction, i.e. diffuseness caused by departure from the crystalline order and diffuseness caused by the small size of otherwise perfect crystallites. On account of these factors, the concept of crystallinity is being displaced by the concept of lateral order distribution which can be defined as follows: Let us choose a volume V within the cellulose which is larger than several unit cells of cellulose, but still so small that further reduction in volume will not change the nature of the distribution curve which will now be defined[17]. Let n_i be the number of hydrogen bonds of cellulose actually present within the volume V and let n be the number of bonds which would have been present if the volume had contained a perfect crystal of cellulose. The ratio $q_i = n_i/n$ will be called the degree of lateral order within the volume V. If now V were to sweep out the entire mass of cellulose actually under investigation, we would determine the frequency distribution of the qis, i.e. the lateral order distribution curve. Obviously, there is no single experiment (physical or chemical) which allows one to map out this distribution. The nature of the curve can only be surmised by putting together all available data on X-ray crystallinity, accessibility to various types of molecules and reactivity to various chemicals. This concept of the order distribution curve is now two or three years old. In the year under review, the concept has been somewhat modified in order to be valid against the
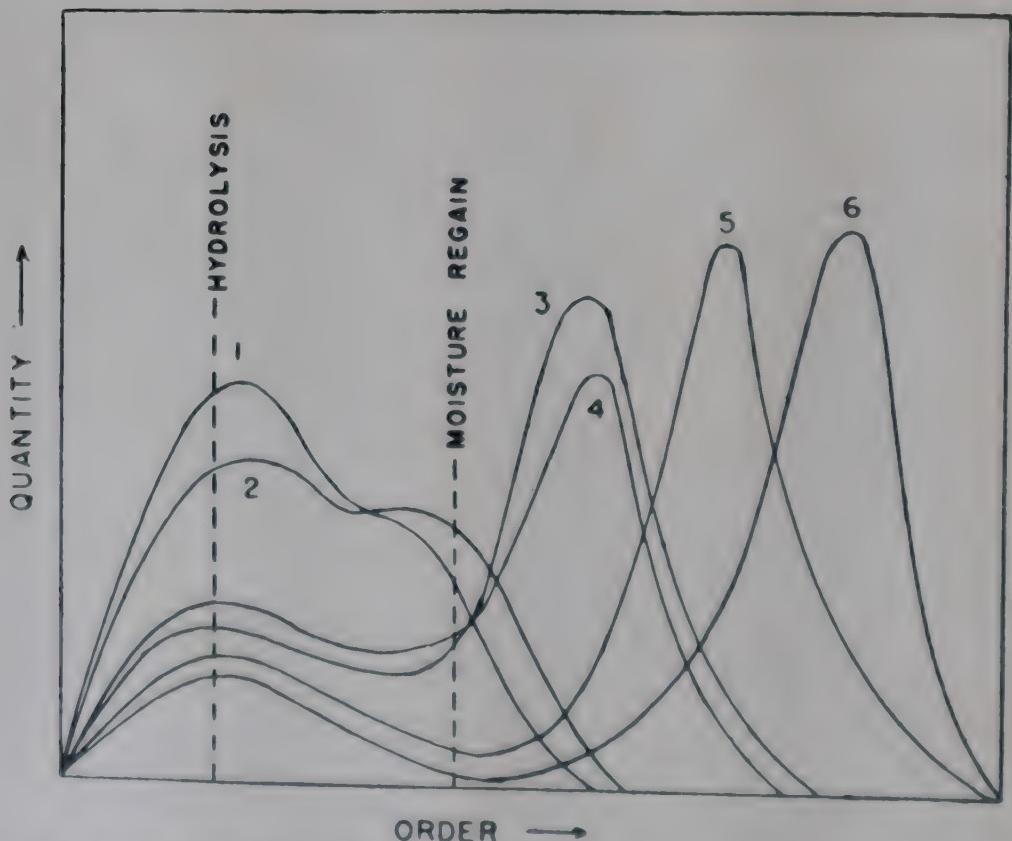
FIG. 2—LATERAL ORDER DISTRIBUTION CURVES FOR VARIOUS CELLULOSE FIBRES [(1) HIGH TENACITY RAYON ; (2) TEXTILE RAYON ; (3) HIGH STRENGTH, LOW ELONGATION RAYON ; (4) MERCERIZED NATIVE FIBRE ; (5) WOOD PULP ; AND (6) COTTON] BROKEN LINES SHOW ORDER LEVELS AT WHICH MOISTURE REGAIN AND HYDROLYSIS METHODS DISTINGUISH THE CRYSTALLINE FROM THE AMORPHOUS MATERIAL
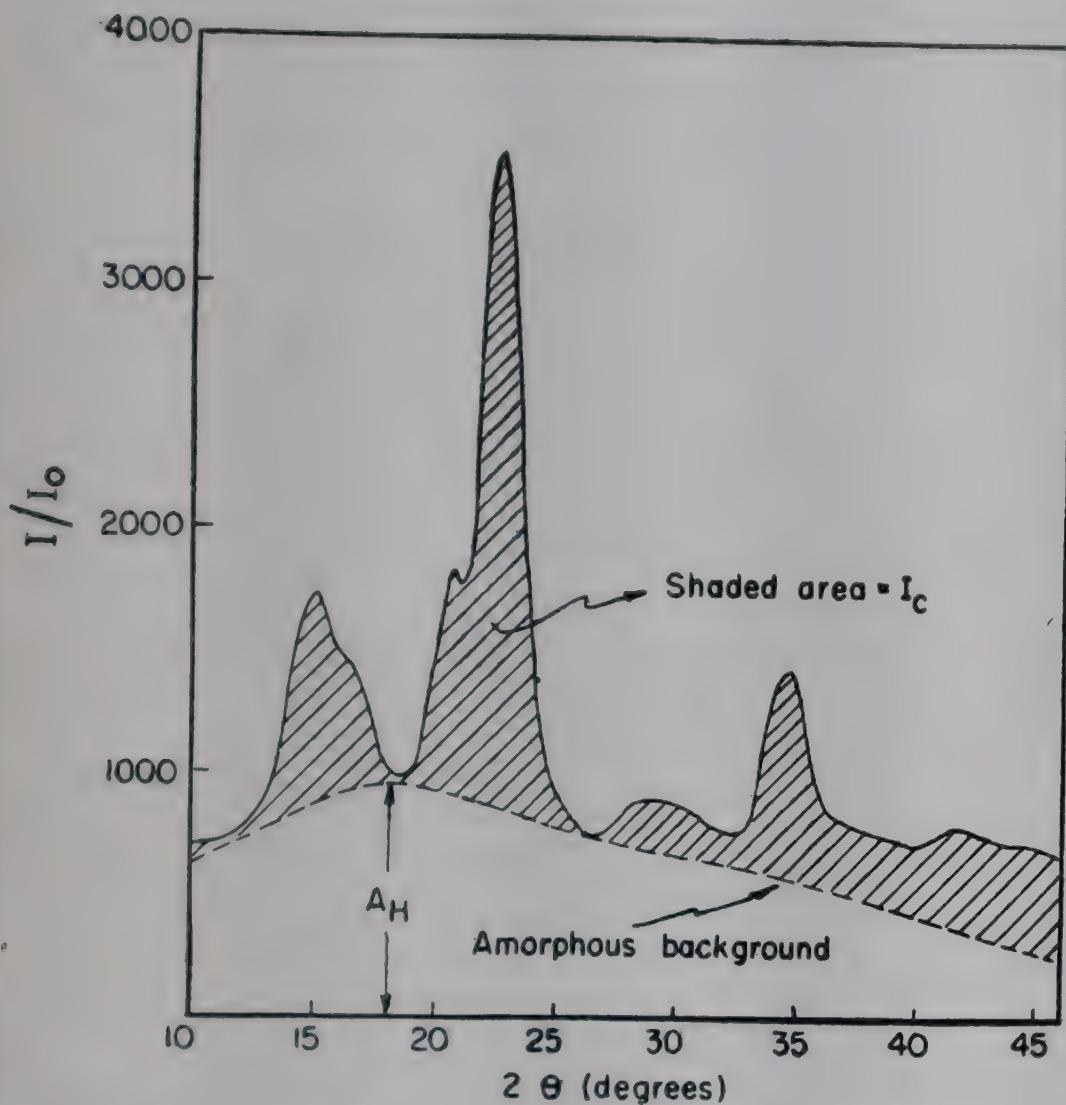
FIG. 3—EVALUATION OF CRYSTALLINITY (Hermans and Weidinger's method)

criticism that all hydrogen bonds may not contribute equally to the cohesive energy of a given volume. Order is now defined as the ratio of the cohesive energy within the volume V to the cohesive energy which a perfect crystallite of cellulose having the volume V would possess. Curves of lateral order distribution (so defined) have been computed from the results of a large number of physical and chemical methods[13] (Fig. 2).

New methods of determining crystallinity—Till recently the standard method was to take a radial trace of the X-ray diffraction photograph from a dis-oriented sample and to compare the area included in the crystalline inter-ferences with the height of the amorphous background after making due corrections for air and Compton scatter, thermal vibrations, etc. During 1955-56 considerable simplification of this method has been proposed[14]. The basis of this simplification is that the line breadth of an interference (for instance, the strong 002 arc) is a measure of disorder or amorphous content. The actual calculation of crystallinity is illustrated in Fig. 3. Fig. 4 shows the Ant-Wuorinen method of determining crystallinity.

It will be clear that this empirical method does not claim to give an absolute value of crystallinity ; besides, it depends on the determination of a total blackening line and is not therefore useful in non-film methods of measuring intensity.

A third X-ray diffraction method[15] for measuring crystallinity has been published during the year. This method requires the measurement (pre-ferably by Geiger counter) of the radial diffraction intensity curves $(I_{2\theta}/I)$ for (*i*) the sample under investigation, (*ii*) a sample of perfectly crystalline cellulose (I or II as the case may be), and (*iii*) a sample of amor-phous cellulose. All these curves should be corrected for counter dead time
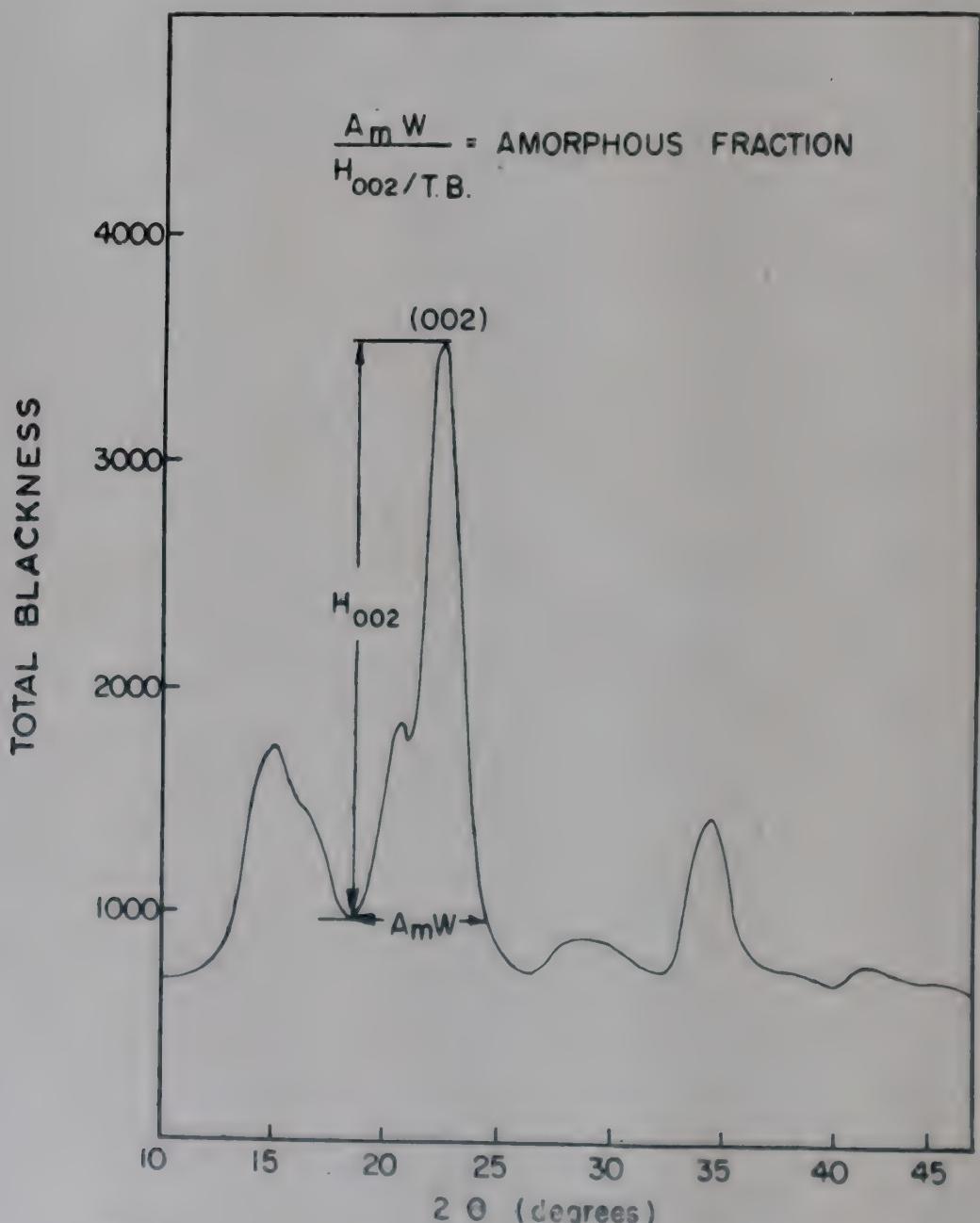
FIG. 4—EVALUATION OF CRYSTALLINITY (Ant-Wüorinen's method)
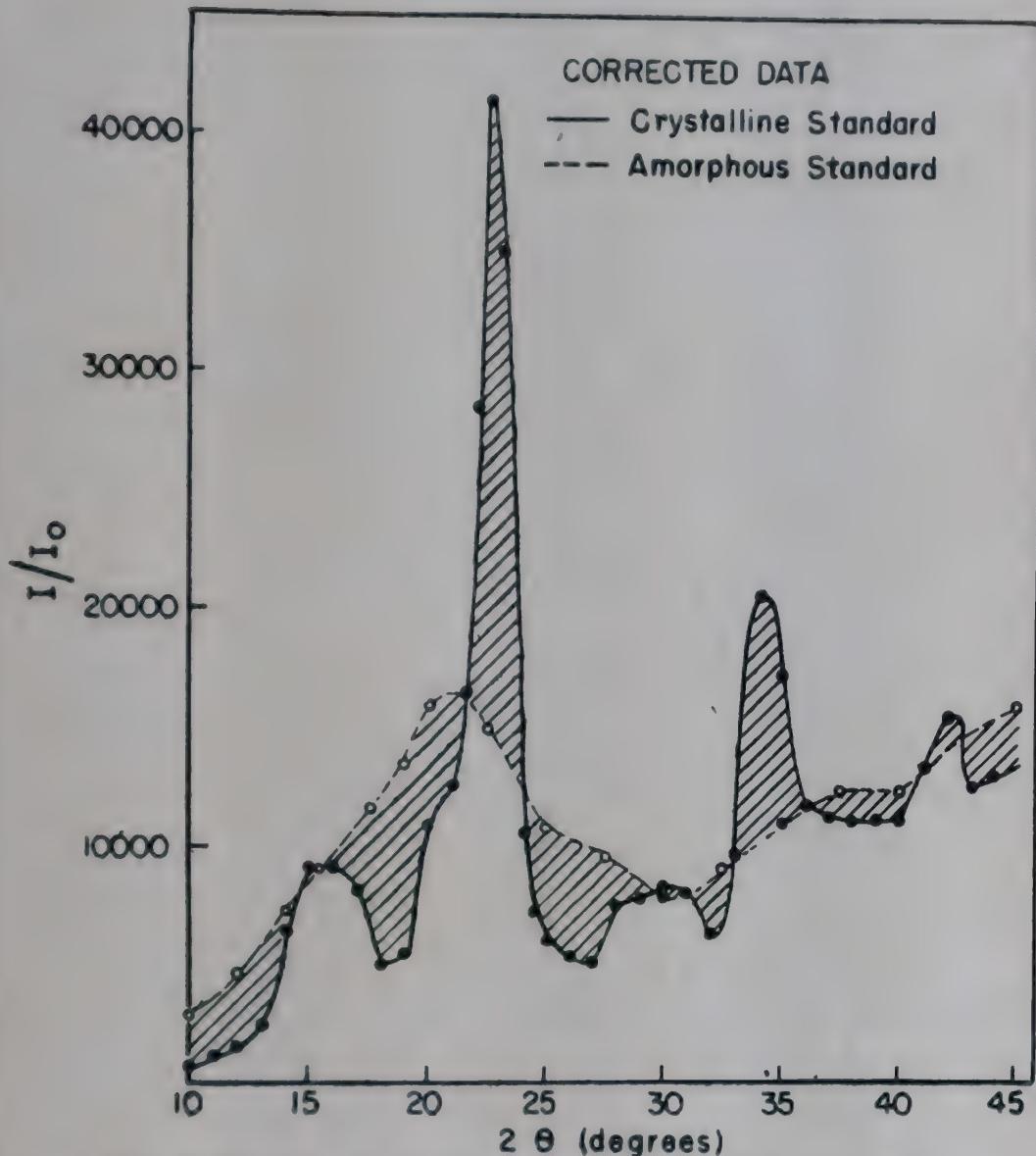
FIG. 5—EVALUATION OF CRYSTALLINITY (Included area method)

losses, thermal effects, air and Compton scatter, etc., and all are to be nor-
malized so that the integrated diffracted intensity over the range covered
(0 to 80°) is the same. Let now, S, C, or A refer to the corrected valves
of $(I_{2\theta}/I_0)$ for the sample, for crystalline cellulose and for amorphous
cellulose respectively. The authors suggest that crystallinity can be defined
as either (i) the included area

$$\left[\int(S-A)\ d\theta\right]\div\left[\int(C-A)\ d\theta\right]$$

or (ii) the slope of the regression line obtained by plotting the pairs of points
$(S-A)_{2\theta}$ and $(C-A)_{2\theta}$ for each 2_θ. Fig. 5 illustrates the determination
of crystallinity by the included area method.

In this case, the correlation coefficient between the two sets of data $(S-A)$
and $(C-A)$ is a measure of the reliability of the data. The two methods
give results which are in good accord. The crystallinity of several samples

of native cotton is found to lie in the range of 65 to 75 per cent. There appear to be some real differences among the various cotton samples examined.

There are a few other papers on crystal structure and crystallinity determinations by X-rays. One of them discusses the structural model of cellulose II chain[16] while another[17] deals with techniques of sample preparation which will minimize errors due to sample size and preferential orientation in the determination of crystallinity.

There has been a considerable volume of important work in the last two years on the determination of crystallinity by physico-chemical methods, such as the deuterium exchange technique[18] and moisture sorption[19,20]. These are not, however, strictly within the field of this review.

Orientation

Since cellulose fibres are uniaxial, the molecular orientation is completely specified by the frequency distribution of the angle made by the molecular chains with the fibre axis. X-Ray diffraction methods in theory permit the determination of this distribution for the chains in the crystalline region only. In practice, even this is difficult, but an average orientation angle for crystallites can be obtained from which the orientation factor can be calculated. These calculations are made on the basis of measurements of the angular variation in intensity of the strong equatorial interferences of cellulose. Present-day methods of recording these intensity variations make use of Geiger counter X-ray diffractometers. An improved version of an angular-scanning diffractometer, using Coller slits, was described last year[21]. This instrument is capable of about double the precision which has been achieved with earlier film methods.

Using Geiger counter diffractometry, the X-ray angles of a number of cottons ranging from the most oriented to the least oriented species observable in nature have been determined and the results correlated with mechanical properties. Further details on this will be given when dealing with mechanical properties. In addition to cotton, the orientation in wood cellulose has also been investigated by some Russian workers[22,23]. Sen and Chowdhry[24] have measured the orientation factor for jute fibres and Stern[25] has measured the orientation factor for coir. These last studies are again correlated with mechanical properties.

Micellar and intermicellar structure

A review of this subject was published last year by Frey-Wyssling[10]. There appears to be little by way of recent original work on micellar structure[26], but a paper[27] on small angle X-ray scattering of viscose which appeared in 1956, presents a new facet to the long inter-particle interference controversy

which has risen round the interpretation of small angle X-ray scattering of cellulose. It is argued that in a densely packed micellar network, the few voids which are present should scatter much more intensely than the material itself. The equatorial small angle scattering is interpreted mostly in terms of these voids and it is deduced that for viscose rayon there is a spectrum of void sizes from 20 to 280 A. Also, it is shown that the meridional scattering from viscose exhibits evidences of a long range periodicity which varies from 170 to 280 Å for different viscoses.

Chackraburtty[28] has published an interesting account of the determination of pore or inter-miceller sizes in the cellulose of nettle fibres, using the well-known technique of deposition of gold and silver in the interstices and photometry of the stained cellulose He concludes that the pore sizes are of the order of 90 Å.

MECHANICAL PROPERTIES

This subject can be considered under three heads: (*i*) Theoretical studies of rheological behaviour, (*ii*) experimental determination of viscoelastic constants, and (*iii*) interpretative correlation between fine structure and mechanical behaviour.

Rheology—Among the theoretical studies of rheological behaviour, only two papers[29] appearing in 1956, are selected for review on account of their importance. The author derives a general stress-strain equation valid for small tensile strains in any hydrogen-bonded solid ; the equation is: $f - E\sigma - K\sigma^2$ where f and σ are the stress and strain, E is Young's modulus and K is a second co-efficient of elasticity. It turns out that both E and K can be expressed in terms of the parameters of the hydrogen bond. Also, K is found to be a general constant, which is independent of the particular structure or degree of order of the hydrogen bonded solid, while E varies from solid to solid by virtue of differences in the average volume occupied by a strained hydrogen bond. Further, the maximum possible value for E on the basis of hydrogen bonding alone, turns out to be of the order of 10 dynes/sq.cm. The constancy of K and the upper limit to the value of E are confirmed by available data on the rheological behaviour of newsprint, kraft paper, viscose fibre and nylon. The influence of temperature and the initial influence of regain on Young's modulus can also be predicted by a further extension of the theory.

Banerjee and Sen[30] have attempted to estimate the average spacing of structural imperfections or weak links in jute and ramie from a measurement of fibre tensile strength and its dispersion at various gauge lengths. However, the dispersion of tensile strength has been determined on the basis of as few as 50 measurements of strength, which appear inadequate on account of the large coefficients of variation involved (30 to 40 per cent).

EXPERIMENTAL WORK

The chief experimental contributions during the period under review are by three groups of British workers who have investigated the influence of temperature and moisture on rupture properties and elastic moduli of cellulosic fibres.

Clark *et al.*[31,32] have determined the values of rupture load, extension at break and stress relation properties of wet viscose yarn over a range of temperatures from 0 to 100°C. As expected, the rupture load decreases and the extensibility at first increases with increasing temperature. But there is a sharp discontinuity in the rupture load versus temperature curve in the range of 50-60°C. Moreover, the extensibility of wet viscose is a maximum in this temperature range. Elastic properties, like stress relaxation and elastic modulus, do not seem to show this type of temperature effect.

Guthrie[33] deals with the effect of temperature on the initial Young's modulus of wet cotton, viscose and high tenacity rayon. In all cases, the act of wetting at room temperature reduces the moduli to about a twelfth of the air-dry value. When the wet fibres are heated, there is a further, but much smaller, fall in elastic modulus. All this confirms that humidity has a much greater plastisizing effect on fibres than temperature. In fact, the author shows that dry viscose in liquid paraffin at 140°C. has ten times the elastic modulus of wet viscose at room temperature. Similar, though less marked, effects exist in cotton.

Meredith[34] describes the effect of moisture sorption on the torsional modulus or rigidity of cellulosic fibres. As expected the torsional modulus G decreases with increasing moisture content M. For all the fibres investigated (cotton, mercerized cotton, ramie, viscose, and fortisan) the change is expressed by the same general formula, $ln\ (G/G_{65}) = -0.82\ (M/M_{65} - 1)$ where G_{65} and M_{65} are respectively the rigidity and moisture sorption of the particular fibre at 65 per cent relative humidity (R.H.). A theoretical explanation of this equation has been offered.

Hertel[35] has carried out a detailed study of the effect of cotton fibre length versus test length on fibre strength.

CORRELATION BETWEEN FINE STRUCTURE AND MECHANICAL PROPERTIES

As a result of the experimental and interpretative work done last year, our ideas on two subjects, namely the effect of molecular orientation and adsorbed moisture on elastic, and tensile properties have sharpened.

Molecular orientation—The correlation between X-ray angle and tensile strength of cotton fibres has long been known. Rebenfeld and Virgin[36] have published, last year, the X-ray angles of a large number of cottons covering the known span of orientation in cotton. Values of single fibre breaking strength, elongation and elastic modulus as well as fibre bundle strength at various gauge lengths, and the count strength products of yarns made from these fibres were also available. The authors estimated the correlation between these properties and the X-ray angle. The bundle strength at zero gauge length showed a correlation coefficient of -0.92 when plotted against X-ray angle. At higher gauge lengths, this correlation became poorer. The breaking elongation and initial elastic modulus of single fibres were also found to be well correlated with X-ray angle ($\rho=0.86$ and -0.82 respectively). The single fibre breaking stress was very poorly correlated ($\rho=-0.49$) with the X-ray angle, a result which can be understood in terms of the weak link theory.

Similar work on jute has been published by Sen and Chowdhry[24]. There appears to be excellent correlation between the intrinsic tensile strength and crystallite orientation factors of a number of jute samples. This is all the more remarkable since the range of orientation factors is 0.96-0.97. The X-ray diffraction diagram of coir[25] shows cellulose micelles to be spirally arranged at high pitch of about 45° to the fibre axis[26]. The high extensibility, initial Young's modulus and other viscoelastic properties of coir can be at least qualitatively explained on the basis of the tensile deformation of the helical structure, i.e. changes in spiral angle during stretching.

Mention may also be made of investigations by Yurugi[37] on the reorientation of viscose model filaments by swelling, stretching and de-swelling and the marked relation which was found to exist between orientation and tensile properties.

Effect of moisture

The general relation between torsional rigidity and moisture content of cellulosic fibres has been described[34]. A very successful attempt has been made to deduce this relation on the basis of the two-phase theory of water absorption[15] after modifying the theory to take into account the different amounts of accessible material in different fibres. It is assumed that the shear modulus of hydrogen bonds is reduced by a fixed fraction by water which has been absorbed to form a hydrate (*a*-phase), while water which is mechanically held in voids (*b*-phase) has no effect on shear modulus. With these assumptions it turns out that the relative rigidity varies linearly with the amount of *a*-water adsorbed. This, in turn, depends in an exponential manner on the total sorption, so that the logarithm of the relative rigidity becomes proportional to the relative moisture content, as observed.

It has been previously mentioned that the tensile properties of wet viscose show some unusual features at 50 to 60°C. This has been explained, in a qualitative manner, on the assumption that this temperature range is attended by a sharp change in the rate of dissociation of cellulose-cellulose bonds.

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Chairman's Address

M. K. SEN

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Cellulose in the idealized sense, is a linear macromolecule in which a large number of glucose units are combined together with primary valence linkages. The average number of glucose residues varies according to the source of cellulose.

Although many of the properties of cellulose are readily explainable on the basis of its molecular formula, some are not ; and the relation between some of these properties and its chemical structure is not very obvious. This is particularly true of the physical properties, such as fibre structure, solubility and mechanical properties. Even the chemical properties are so dependent upon physical factors that it is sometimes difficult to see the connection between the behaviour of cellulose in its reactions and the chemical formula. It is, therefore, necessary to consider the nature of the intermolecular attraction between cellulose chains in order to obtain satisfactory explanation of many phenomena that are observed. Many of the complications encountered in cellulose chemistry are due to the fact that the intermolecular forces between cellulose chains can produce a supermolecular texture or type of arrangement which profoundly influences most of the properties of the material. Once created, a particular arrangement is rather difficult to alter. Chemically similar celluloses may therefore exhibit very different properties.

The first stage in the recognition of the possible nature of the texture or supermolecular structure of cellulose came with the discovery that cellulose gives well-defined X-ray diffraction diagrams. Further progress came with the realization of the connection between mechanical properties and the ordered arrangement revealed by X-rays. But although attention was first focussed on the sharper interference spots which indicated the existence of domains where the chain molecules were ordered in three dimensions in a degree of perfection approaching that of the crystalline state, it was soon realized that only a portion of cellulose fibres could be considered as belonging to these crystalline regions. The concept arose that the crystalline regions

were embedded in an amorphous matrix and the highly ordered domains could be considered as establishing cross-links between the less ordered regions, capable of preventing slippage on the application of a load. The regions of low order, on the other hand, appeared to be responsible for such phenomena as swelling in solvents and the continued deformations or creep encountered under the influence of a sustained stress.

In order to characterize the complex dual structure of discontinuous crystallinity in which the crystals are separated by more or less disordered material coupled with the usual orientation of the crystallized regions in respect to some simple dimensions, it is necessary to consider (i) the spatial arrangement of the atoms within the molecules and the spatial arrangement of the molecules within the crystallites ; (ii) the size, shape and distribution of the crystallites ; (iii) the relative proportions of the so-called crystalline and the non-crystalline phases ; and (iv) the orientation of the crystalline and the non-crystalline phases with respect to one another and to the fibre surface.

Crystal form

Four crystalline modifications of cellulose have so far been reported. All natural cellulosic materials including bacterial and animal cellulose with the possible exception of the marine plant *Halicystis* show identical crystalline structure. This crystal form is usually called the native cellulose or preferably cellulose I. If cellulose is dissolved and precipitated from solution or regenerated from some addition compounds of cellulose I, such as alkali cellulose which is formed in mercerization, the molecules reassemble into an allotropic modification which is known as hydrate, mercerized or regenerated cellulose or cellulose II. The existence of the other two forms of cellulose, viz. cellulose III and cellulose IV, is rather controversial. According to one school, it is not necessary to consider cellulose III and cellulose IV as true polymorphic forms, and without introducing any errors of consequences, cellulose IV can be regarded as a disordered form of cellulose I, and cellulose III as a disordered state approximating to cellulose II. Of the four forms of cellulose, the crystal form of cellulose I has been the subject of most extensive investigation and next to that the structure of cellulose II. The most widely accepted view is that these materials have monoclinic unit cells belonging to the space group P_2. According to this picture, cellulose may be regarded as a combination of a chain lattice and a layer lattice, composed of primary valence forces along the chain axis, relatively strong hydrogen bond network in the plane of the pyranose rings, and weaker van der Waals forces perpendicular to these planes. Although many properties of cellulose in the solid state are explained by this structure, it cannot, however, be regarded as unequivocally established and a straightforward Fourier analysis of the X-ray diagrams is still lacking. It has, therefore, been challenged on several occasions, particularly on the basis of the appearance of X-ray reflections forbidden by the unit cell or of

calculated intensity discrepancies. Recently, two or more new reflections have been detected in samples of some cellulosic materials which are found to be sensitive to moisture content ; and assuming them to originate from cellulose crystallites, new unit cells have been suggested for native and mercerized celluloses. While the new reflections, especially the one with the larger spacing has been confirmed in jute by several workers, refined experimental arrangements seem to be necessary for establishing them in pure cellulosic materials, such as ramie or cotton. In this connection, it is also relevant to point out that acetylated ramie and cotton diagrams show an intense, though rather broad, reflection near about this region, and one wonders whether this reflection refers to the plane corresponding to the newly discovered larger spacing. In addition to the new reflections, the X-ray diagrams of jute and other fibres which contain a considerable proportion of non-cellulosic materials, such as hemicelluloses and lignin, also show certain other characteristics. For example, the reflections in jute are more diffuse laterally than in ramie or cotton ; the reflection 101 and 10$\bar{1}$ are not resolved even in photographs of moderate intensity ; the 101 spacing is slightly smaller than that of standard cellulose ; the reflection 020 is more intense than in ramie and under normal conditions raw jute does not undergo complete transformation from cellulose I to cellulose II. While these features can be tentatively related to noncellulosic inclusions, particularly hemicelluloses and lignin which might be responsible for mixed crystallization, lattice distortions, etc., elaborate studies may lead to useful information regarding the influence of relative amounts of cellulose, hemicelluloses and lignin and the growth and maturity of fibre upon structure.

Notwithstanding the fact that only a portion of the cellulosic material is in the crystalline state, attempts have been made from time to time to find a correlation between the physical properties and the various transformations of cellulose from one crystal form to another. It was, however, soon realized that change in macroscopic properties, such as moisture absorption, dye absorption, swelling, tenacity, and elongation, accompanying mercerization or procedures involving solution and reprecipitation of cellulose is not due to the presence of cellulose II but to decrease in the amount of crystalline material and crystal size, change in crystalline orientation, etc. In view of these observations, the various polymorphic modifications of cellulose are now regarded as interesting but accessory phenomena.

Crystallized regions

The abnormal breadth of the X-ray interferences in cellulose diagrams suggests that besides the small size of the crystallized regions, other factors, such as strain in the crystal, impurities or imperfect crystallization, might also be responsible for the phenomenon. For this reason, the estimate of crystal size by the method of line-broadening is regarded as only very approximate and the method which is now used for the determination of

particle size, shape and distribution utilizes the evaluation of low angle
X-ray scattering near the direct beam.   But although the low angle scattering
method is relatively independent of most structural elements other than
particle characteristics, it is experimentally difficult, and the theory necessary
for interpreting the results is not altogether free from ambiguity.

In order to give a quantitative significance to the small angle scattering
it is necessary to determine the variation of scattered intensity with the
scattering angle.   The theoretical relationship of this curve to the dimen-
sions of particles can be calculated on the basis of certain hypotheses regarding
the system of particles and on the principle that the small angle scattering
originates from the difference of electron density between the particle and
an equal volume of the external medium in which the particle is embedded.
In the particular case of oriented particles, e.g. micelles in the shape of
ellipsoids having their long axes parallel, the shape of the particle can
be deduced from the shape of the scattered pattern.   But complications
arise either when the particles are not identical but of irregular size or when
they are not well separated from one another.   It is not possible to obtain
the distribution of particles of different sizes directly by the analysis of scat-
tering curves.   But by postulating a law of distribution containing an
arbitrary parameter, the corresponding scattering curves can be calculated
theoretically and the parameter adjusted to give the best agreement with
the experiment.   This allows one to decide whether the system is composed
of different sized particles to give a numerical value to the dimensions of the
largest particles in the system and to outline roughly the distribution of
the different particle sizes.   In a dense system, the intensity is considerably
modified as a result of interference between the resultant waves from the
different particles.   When the system is not too dense, the intensity is
diminished because of interference but the slope of the curve as a function
of the angle is not appreciably modified.   But if the apparent density of
the specimen is close to the real density of the particles, it becomes very
difficult to obtain true quantitative results from the pattern.   This compli-
cation arises in the case of most fibres in which the microcrystallites are
very close to one another and the radiation from neighbouring particles
generally interferes.   Heyn, in a series of papers, claims to have shown
that the swelling method offers a mean of separating independent and non-
independent scatter and that under certain conditions of swelling, inde-
pendent particle scattering is realized and from the scattering under such
conditions, the particle size in different fibres is determined on the basis of
the theoretical formulae for independent scattering.   But the straight
logarithmic nature of intensity curve, obtained by him and regarded as
indicative of independent particle scattering, has not been confirmed by
Heikens et al.   The latter have also observed some unexpectedly remark-
able results that the scattering curves of certain artificial rayons show well
defined maxima, which is apparently indicative of a sufficiently regular

structure in those fibres. Moreover, Heyn's results on swelling of jute and ramie do not appear to have any correspondence in the microscopic regions. As for example, the results imply that the degree of interparticle swelling in ramie at 1 per cent alkali is not realized in jute until the concentration of alkali is raised to 5 per cent, whereas the available evidence on swelling indicates the reverse. Recently, Stern has studied the variation of the small angle X-ray scattering power of ramie and jute fibres containing moisture and compared his results with the theoretical values calculated on the basis of a mechanism postulating moisture take-up by cellulose. He has, however, observed some discrepancy in that the theoretical scattering power of the wet fibres is much greater than the experimentally determined value.

In view of the above considerations, it seems worthwhile to examine the interpretation of the small angle X-ray scattering by cellulose materials. A considerable volume of research has been devoted to the subject and some important data are already available for various materials including jute. It seems that these results can be usefully confirmed and amplified. A similar fruitful line of approach is through electron microscope studies. The electron microscope has the advantage of directly examining the chemically degraded or ultrasonically dispersed cellulose systems. The evidence obtained so far points to the important conclusion that while pure cellulose fibres, such as ramie and cotton, disintegrate into elongated, tubular, ultimate particles of the same order of mean lateral size as that which has been accepted as characteristic of the crystallites in cellulose from X-ray evidence, the mode of disruption of lignified fibres (e.g., jute) is essentially fibrillar rather than particulate in nature and lignin is involved in the stability of the fibres against acid attack.

Crystalline-non-crystalline proportions

The background which is found to be always present in the X-ray photographs of fibres at once indicates the presence of a considerable amount of non-crystalline material in cellulose. Unlike the crystalline regions, the non-crystalline area cannot however be defined as one in which the chain molecules are in a complete lack of order. This region should rather be considered to contain all possible degrees of packing between the liquid state and the crystalline state. In view of the great importance of the non-crystalline areas in affecting most of the properties of fibres, a large number of methods has been proposed for the determination of the relative amounts of crystalline and non-crystalline materials in cellulose. Among the physical methods, the X-ray method has been the most important in estimating the proportion of crystalline cellulose. This is based on the assumption that the relative intensities of the discrete reflections and the background should depend on the proportions of the two components present. The application of this method to jute indicates that the percentage of cellulose crystallites in this fibre, calculated on the basis of alpha-cellulose content, is

the same as in pure cellulose fibres, suggesting that the strong background radiation in jute fibre X-ray diagram is mainly due to the amorphous non-cellulosic constituents. The presence of a greater proportion of amorphous noncellulosic material in jute is also indicated from the results available from moisture relationship, heat of wetting, sorption ratio, swelling in water and swelling and solubility in alkali. The evidence available from the mechanical properties of jute indicates that the intercrystalline regions of the fibre constitute a framework of cellulose-lignin-hemicellulose interspersed with cross-linkages and a greater number of hydrogen bonds, some of which may be of higher energy. This probably explains the appreciable difference between jute and ramie as regards the type and degree of imperfections recently observed. In this regard, infrared spectroscopy may throw further light.

In view of the consideration that most of the physical properties of cellulose fibres are greatly influenced by the non-crystalline areas, a more extensive investigation of the non-crystalline areas seems urgent. At the same time, proper characterization of the structural arrangement is also equally important. For, although the existing methods show a definite trend in placing the various samples of cellulose according to their relative crystallinity order, none of them yields absolute values in defining a cellulose structure. Recently, the structural arrangement has been very effectively described for cellulose in terms of "mass versus order", and "orientation versus order", representing the complete molecular arrangement of the total mass from the amorphous to the perfectly crystalline state. The mass-order distribution curves constructed from the available data show that jute is characterized by the presence of a high proportion of material of very low order, a result which has been previously indicated in a rather qualitative manner.

Orientation

The co-existence of ordered and disordered phases of fibre structure as discussed before makes the study of orientation in cellulose materials involved and complicated. In the widest sense, the term orientation should refer to the alignment of individual molecules relative to one another and to the surface of a sample. But in this sense, the term does not lend itself to quantitative expression. Orientation is now most often used to refer to arrangement or alignment of crystallized regions in respect to the fibre axis or to the fibre surface. The crystallite orientation will obviously determine the orientation of the component molecules, whereas the orientation of individual molecules within a non-crystalline region may vary from point to point and from fibre to fibre. Quantitative expressions for the orientation of molecules within a fibre have been derived from birefringence and dichroism of dyed fibres and films, but their physical significance is not yet clear. Quantitative X-ray method for the estimation of cellulose crystallite orientation, on the other hand, forms the basis for most methods now in use. The exact measure-

ment of orientation in many natural fibres is however complicated by the morphology of these fibres. Natural cellulose fibres have been found to be characterized by orientation ranging from nearly perfect parallel fibre structure to almost completely random arrangements. The bast or soft fibres are generally characterized by orientation almost parallel to the fibre axis. The spiral angle is of the order of $5°$ and deviation of fibril orientation from this angle is small. The orientation of jute fibres vis-a-vis ramie has been investigated by both optical, swelling and X-ray methods. While the results of X-ray investigation indicate that jute has slightly lower orientation than ramie, those of the optical method suggest an appreciably large difference between the two fibres. The swelling method, on the other hand, indicates a high orientation of the chain molecules in the non-crystalline regions, and the dependence of the crystallite orientation on the intercrystalline domains. The latter is also indicated from the results on shrinkage of jute in alkali. Future investigation on orientation of jute and other similar fibres may be directed towards the influence of growth on the progress of orientation and in this regard, work with single fibres and microbeam technique may lead to useful information.

The influence of orientation on the physical properties of cellulose fibres, particularly with reference to tensile strength, elasticity, dyeing properties, elongation, swelling, etc. has been investigated by many workers. It has been found that by using a quantitative X-ray method for measuring orientation, a close linear correlation is obtained between orientation and tensile behaviour, tenacity and elongation. As a general rule, tenacity increases linearly, while elongation decreases exponentially with increasing orientation, but there are deviations from this, particularly in the case of regenerated fibres and the effect of lateral order in this regard is very considerable.

Finally, it is needless to point out that because of its complex character, a complete and unequivocal elucidation of cellulose structure is not yet possible. Most often, the material does not lend itself to a straightforward experimental procedure, nor are the results amenable to direct theoretical interpretation. However, valuable information regarding structure can be obtained from investigations using different preparations of material and more refined techniques.

Decrystallization of Cotton Cellulose

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Methods adopted for decrystallization of cellulose fibre have been reviewed. Treatment with anhydrous ethylamine, the best of the methods for decrystallization, difficulties encountered in large scale adoption of the method, attempts to understand the mechanism of the treatment and the effect of decrystallization on the physical properties of cotton fibre have been outlined.

Cellulose consists of long chains of glucose residues which contain a large number of hydroxyl groups. These groups exert intermolecular attraction and bring about cohesion of the adjacent chains by hydrogen bonding. Association of a number of chains lying side by side in one plane may contribute to a two dimensional lattice in which the hydroxyl groups are blocked for any reaction ; while the three dimensional orderly packing of the chains which are held together by such intermolecular forces contribute to the crystalline structure as exhibited by X-ray diffraction photographs. The places where the chains are lying in a disorderly manner, not being associated with one another, are called amorphous regions.

The crystalline structure is to some extent responsible for the tensile strength of the fibre, whereas the amorphous regions allow for internal flexibility and contribute to the elongation and elastic properties of the fibre. Cellulose present in natural fibres possesses a high degree of crystallinity which, while contributing to tensile strength, is responsible for stiffness and brittleness due to lack of flexibility[1].

Attempts have been made to reduce partially the crystallinity of cotton fibres with the object of overcoming these defects and bringing about changes in the elongation and elastic properties[2]. It is also claimed that properties, such as tear strength and wear life, which are valuable to fabrics would improve as a result of decrystallization[3]. The other advantage of reduced crystallinity is the increase in accessibility to reagents thereby improving its dyeing capacity and chemical reactivity.

METHODS OF DECRYSTALLIZATION

Mercerization with caustic soda is known to effect some reduction in crystallinity and alteration of the crystal lattice into that of hydrated cellulose II. Though considerable swelling occurs in the formation of soda cellulose, re-association appears to take place after washing out the swelling agent and drying the material. The net fall in crystallinity is, however, very small especially if it is worked under tension. Recently, some commercial success has been achieved in preparing bandage cloth possessing high elongation and semi-elastic properties by slack mercerization of cotton gauze and by washing and drying the material without tension[4,5].

Several other swelling agents, including the quaternary ammonium hydroxides, have been tried. But many of them have a relatively narrow range for their swelling concentration and the concentration at which dispersion takes place.

Special attention may be drawn to the work of Davis et al.[6] who found that treatment of cotton cellulose with liquid ammonia and certain aliphatic amines alters the lattice structure of cellulose, somewhat similar to hydrated cellulose after caustic soda treatment.

Segal et al.[2,7], who may be credited as the pioneers in the work of decrystallization, have carried out detailed investigations with various amines and have found that anhydrous ethylamine is the most efficient chemical in lowering the crystallinity. They have claimed that the crystallinity is lowered to 20-30 per cent without damaging the fibre structure or affecting the desirable physical properties already possessed by cotton.

The method consists in treating cotton with anhydrous ethylamine, the material being kept out of contact with air to prevent oxidative degradation, in loose or relaxed condition, for nearly 4 hr and subsequently extracting the amine with chloroform.

They observed that the amine homologues above propylamine are not capable of swelling cotton fibre directly and bringing about reduction in crystallinity. However, higher amines, like hexylamine and heptylamine, cause reduction in crystallinity after preliminary treatment with ethylamine or in admixture with ethylamine.

They also found that secondary and tertiary amines, like di- and triethylamines, are ineffective in reducing crystallinity even at ice bath temperature and they attribute the failure of these amines to steric hindrance.

It was also reported that the combined treatment of ethylamine and caustic

soda is ineffective as the ethylamine treatment is lost on subsequent treatment with caustic soda because cellulose II predominates the crystal pattern.

As anhydrous ethylamine is a volatile liquid (b.p., 16°C.), refrigeration is required for the treatment. In order to avoid this, vapour phase treatments have been tried, and Greathouse *et al.*[8] have put up a pilot plant for vapour phase treatment at the *Southern Region Research Laboratory*, New Orleans (U.S.A.).

Segal and Loeb[9] recently have tried aqueous solutions of ethylamine for this purpose and have found that solutions of strength above 70 per cent only are effective in decrystallizing, and cooling would be necessary in maintaining these strengths and that the material has to be washed in acetone which mixes with aqueous amine solutions. Aqueous ethylenediamine has also been tried and it is found to be effective above 60-65 per cent strength.

The following points should be borne in mind for the commercial application of this treatment :.

Ethylamine is a costly chemical and as its boiling point is only 16°C. there is need for refrigeration. This complicates the working and increases the cost of treatment. Washing with an organic solvent still further increases the cost. Vapour phase treatment besides being hazardous involves complicated and costly equipment. Hence it is necessary to pursue further research to find a chemical better than ethylamine which will be cheaper and easier to work with.

Estimation of crystallinity—Several techniques, both physical and chemical, have been developed for the determination of crystalline-amorphous ratio ; but among them, the X-ray method and the acid hydrolysis method[10] are the only two which have been extensively employed. These methods are quite elaborate and complicated. Measurement of crystallinity in all these investigations has been mostly carried out by the acid hydrolysis method. This method is more time-consuming and the results become progressively unreliable as the crystallinity drops below 50 per cent[11]. The recent iodine adsorption method [12,13] appears to be quite simple in application and could be employed in these experiments for measuring the degree of crystallinity.

Stability of decrystallization

Maintaining the effect of decrystallization after the removal of the reacting chemical and subsequent wet treatment is a more important problem. Introduction of blocking groups in the place of hydroxyl groups to prevent subsequent reassociation or of cross-links with bigger molecules to maintain the chain apart or distension of the chains permanently, have all been considered ; but not much work has been done on these lines. Segal *et al.* have observed that the decrystallization effect by anhydrous ethylamine

remains stable, at least partially, even if the material is boiled in water, provided the material is freed from the amine by extraction with an organic solvent, like chloroform, and drying. If, however, the amine is washed with a polar liquid, like water, recrystallization occurs. Thus they claim that the introduction of blocking groups is not necessary if decrystallization is effected in the manner described. They have tried subsequent boiling in water up to 3 hr. This point needs to be examined still further. Extensive washing with an organic solvent for the complete removal of amine on a large scale would be very costly and other methods are, therefore, worth attempting.

Effect of decrystallization on the properties of the fibre

Segal, Nelson and Conrad[7] found that yarn decrystallized by treatment with ethylamine under atmospheric conditions showed a fall in degree of polymerization (D.P.) by 16 per cent whereas yarn when treated in air-free condition showed a fall in D.P. of only 3 per cent. Thus it was concluded that oxidative degradation of cellulose could be avoided by the exclusion of air during the amine treatment. They measured the crystallite lengths of the amine treated fibres by determining the D.P. after the levelling off process (hydrolysing with 2.5 N. hydrochloric acid). It was observed that there was a definite fall in the crystallite lengths and the extent of decrystallization. It was also found that crystallite orientation was not altered by ethylamine treatment.

Certain physical properties of chemically modified cottons have been estimated by Grant[14] and are included in Table 1.

It may be seen from the Table that there is an improvement in moisture regain, elongation and secant modulus after ethylamine treatment particularly, in the slack condition. Slack mercerization shows enhanced effects when compared with amine treatment in the slack condition. There is some fall in the length which may be considered as a drawback ; but detailed information in regard to the different degrees of decrystallization and their relation with these and other physical properties of fabrics, like tear strength and wear life, is lacking, the effect of subsequent treatment and the alterations in properties brought about thereby are not known.

MECHANISM OF AMINE TREATMENT

Davis *et al.*[8] have discussed the mechanism of reaction of amines with cellulose and assume that normal hydrogen bonds between hydroxl groups and acetal oxygen of the adjacent chains are broken up and fresh hydrogen bonds are formed between the hydroxyl hydrogen and the amine nitrogen. The interesting fact brought out from the study of X-ray diffraction patterns of treated celluloses was that the 101 lattice spacing of cellulose crystallites

TABLE 1—PHYSICAL PROPERTIES OF FIBRE OF DELTAPINE & ROWDEN COTTONS AFTER CHEMICAL MODIFICATION

	UNTREATED	MERCERIZED & ALLOWED TO SHRINK	RESTRAINED	ETHYLAMINE DECRYSTAL- LIZED & ALLOWED TO SHRINK	RESTRAINED
Crystall- inity, %	80	. .	. .	30	51
Moisture regain, %	6.8	9.4	9.0	7.9	7.4
Density, g./cc.	1.550	1.515	1.536	1.536	1.541
Mean length, %	100 (0.94 in.)	88	97	91	95
Linear density, %	100 (1.88 grex)	110	100	104	102
Breaking load, %	100 (5.5 g.)	123	123	102	104
Elongation at break, %	100 (8.1%)	178	99	127	97
Tenacity, %	100 (2.9 g./grex)	112	123	98	102
Secant modulus, %	100 (36 g./grex)	63	125	78	106

progressively increased from 10.3 Å to 26.2 Å in the ascending order of the amine series up to heptylamine. In spite of such tremendous distension of the cellulose lattice on the introduction of large molecules as heptylamine, no dissolution of cellulose resulted. Failure of such dispersion was connected with the constancy of the 10Ī distance for the whole series of amine cellu- loses. The constancy of the distance indicated some sort of binding of chains in the 10Ī direction. In order to explain such a binding they assumed that the amine group which formed the hydrogen bond with one of the hydroxyl hydrogens by sharing an electron pair might further accept an electron pair from the oxygen of the hydroxyl group of the adjacent chain. This involves the formation of a double bridge of the type O-H.....N-H.....O. Such a bridge would not be possible in the case of the nitrogen of tertiary amine. Other alternatives have also been suggested for the nature of bind- ing but no experimental confirmation has been put forth for these so far. Segal et al.[2] have observed that secondary and tertiary amines are not effec- tive in decrystallizing and it appears that the nitrogen of the secondary and tertiary amines is not strong enough to break open the existing hydrogen bond. Due to the larger size of the higher amines, it is presumed that they are prevented from penetrating the cellulose lattice until it has been opened up to a certain extent by treatment with lower amines. It has also

been observed that monoethanolamine containing the hydroxyl group, like water and alcohol, has no high swelling action on cellulose.

Davis et al.[6] observed considerable alteration in the lattice structure of cellulose as a result of the treatment with liquid ammonia or aliphatic amines and suggested that cellulose III which is somewhat similar to cellulose II is formed.   Segal[15] claims that normal cellulose I structure is maintained after decrystallization treatment with anhydrous ethylamine under conditions mentioned by him.   Mann and Marrinan[16] have also reported that cellulose III structure results after treatment with anhydrous ethylamine followed by extraction with chloroform.   Apart from the difference of opinion with regard to the resulting cellulose structure, cellulose I or cellulose III, it is important to understand the effect of the resulting structure on the physical properties of the fibre.   A thorough knowledge of the mechanism of the reactions which bring about decrystallization would be of great help in choosing suitable chemicals for the purpose.

ACKNOWLEDGMENT

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The Fine Structure of Lignified Cell Wall

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Methods of preparation of wood specimens for electron microscopic examination and some salient features of the fine structure of lignified cell wall of wood as revealed by such a study have been described.

Many properties of wood are dependent in a high degree on the fine structure of the cell wall, i.e. on the arrangement of cellulosic elemental fibrils, and other components like, hemicellulose, lignin and pectin.

The results obtained by the use of light microscope have their limitations in spite of the best optical supplements that could be attached to it. Indirect methods like polarization microscopy, phase contrast and X-ray diffraction are useful in discovering more of the secrets of the cell wall structure, but these methods also have their limitations in revealing the subtle structure of wood. Only with the aid of the electron microscope has it become possible to open this new dimension in the fine structure of wood, because the possible resolution with this instrument is 100 times more than that with the best light microscope. Though electron microscopic investigations are very recent, many new and interesting results have been obtained.

A special difficulty in electron microscopy is the preparation of specimens for examination. The specimens should not be thicker than 0.5μ* as otherwise they are not permeable enough for the electrons. Therefore it is necessary to use special preparation methods. These can be divided into three groups: suspension, thin-section and replica techniques.

Suspension Technique—In this method, the object is chopped and mechanically and chemically reduced to a suspension, the small particles of which can be investigated in the electron microscope. The disadvantage of this method is that the original structure is exposed to intensive alterations and the disconnected building elements have to be interpreted carefully. The method is suitable specially for young non-lignified cell walls, like cambium cells.

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* $\mu = 10^{-4}$ cm. $= 10^4$ Å

Thin-section Technique—The method consists in making extremely thin sections of about 100-200 A* with the aid of a special ultra microtome. Examination of sections without any chemical treatment is useful only for special problems.

Replica Technique—In this method, the area to be examined is supplied with a thin cover of a plastic-like material which is able to comply with the smallest structural particles. Thus a matrix showing the negative relief of the surface structure of the object is obtained. After removing the matrix carefully from the surface of the sample, it has to be shadowed under a certain angle with a metal film in order to intensify the contrast. After this, the matrix material is dissolved and the thin metal film is examined under the electron microscope.

The cell wall is usually built up of the so-called elementary fibrils. These are long stretched units with a diameter of about 100-140 Å. They consist of cellulose macramolecules .In the cell wall the elementary fibrils lie together in bigger units called elementary lamellas. The thickness of the elementary lamella is about 600-700 A. The elementary fibrils and the elementary lamellas are surrounded by substances of amorphous structure, like lignin.

Investigations with light microscope have shown that the cell wall is built up of different layers: the middle lamella, the primary wall, the secondary wall and the tertiary wall which encloses the cell lumen. Special knowledge about the fine structure, however, has been obtained by the electron microscope only. The middle lamella, lying between the cells, consists mostly of lignin and therefore it looks isotropic in a polarization microscope. The electron micrographs, however, show that the middle lamella is not a uniform substance, but in many cases it consists of 2 different amorphous layers, which may enclose also a homogeneous layer between them (Fig. 1). This double lamella construction seems also to be more understandable from the point of view of development than the single layer theory, because for its development the protoplasts of two neighbouring cells must be active. The primary wall, next to the middle lamella, is very thin and can hardly be seen in lignified cells. For its investigation the young cells of the cambium, which have not yet formed a secondary wall, are most suitable. These cells show that the primary wall consists of 2 network-like layers lying one above the other (Fig. 2). Each of them has a different orientation to the axis of the cell. The elementary fibrils of the primary wall are arranged quite far from each other and the space between them is filled with homogeneous substances.

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* $\mu = 10^{-4}$ cm. $= 10^4$ Å
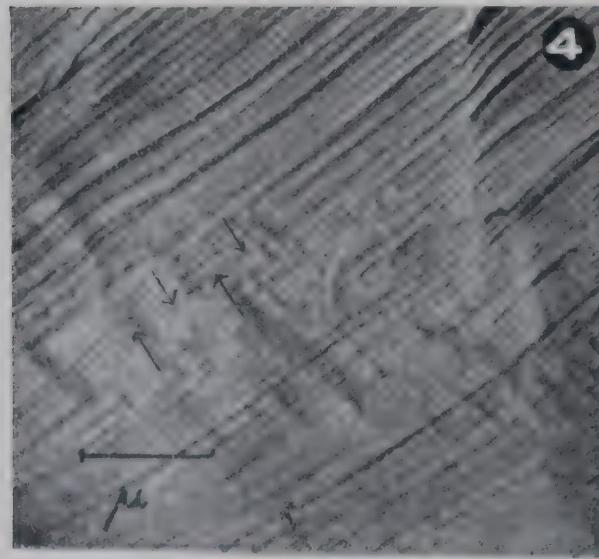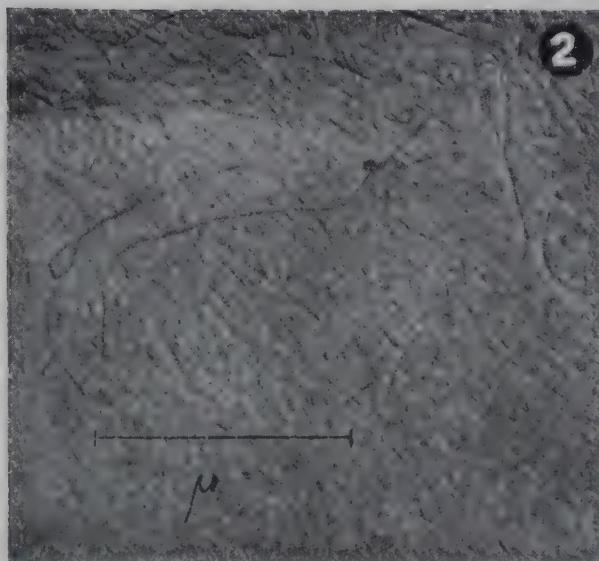
FIG. 1-5. 1—CROSS-SECTION OF MIDDLE LAMELLA OF *Albies alba* (×2,600); 2—PRIMARY WALL, TRACHEID OF *Pseudotsuga taxifolia* (×27,500); 3—CROSS-SECTION OF CHEMICALLY TREATED OUTER LAYER OF SECONDARY WALL WITH THREE ELEMENTARY LAMELLAE (MIDDLE LAMELLA REMOVED) OF *Populus nigra* (×15,800); 4—LONGITUDINAL SECTION OF CENTRAL LAYER OF SECONDARY WALL OF *Pinus rigida* WITH NUMEROUS ELEMENTARY LAMELLAE (×14,200); 5—TOP VIEW OF CENTRAL LAYER OF THE SECONDARY WALL *of Albies firma* WITH THREE DIFFERENT LAMELLAE OF DIFFERENT ORIENTATION (×7,900)

Next to the primary wall is the secondary wall which consists of a small outer layer and a big central layer. Both of them are built up of several elementary lamellas. The outer layer is about 0.25μ thick and consists of three elementary lamellas (Fig. 3). Inside the elementary lamella the elementary fibrils are arranged in a parallel texture. The arrangement of the elementary fibrils in the outer layer of the secondary wall is like a flat spiral with an angle of $80°-90°$ to the cell axis. The orientation of the single elementary lamellas may however be different. The central layer of the secondary wall performs the main part of the cell wall. It is built up of a large number of elementary lamellas (Fig. 4). The elementary fibrils in the elementary lamellas also have a parallel texture. However a scattered fan-like structure is also found sometimes. The elementary lamellas lying one above another sometimes show a coordinated direction of their elementary fibrils, but more often a different orientation (Fig. 5). The secondary wall therefore appears as a plywood-like construction. The predominant direction in relation to the cell axis forms an angle of $5°-30°$. Between the single elementary lamellas there is an intermediate substance and therefore the secondary wall appears lamellated both structurally and chemically. This intermediate substance is important specially for the problem of the stretching of cells.

The innermost layer being the partition wall between the lumen and the cell wall is the tertiary wall which is also sometimes designated as the inner layer of the secondary wall. The tertiary wall is made up of only one single elementary lamella. Very much unlike the secondary wall it has a slightly woven texture (Fig. 6). Further, the tertiary wall is quite different from the secondary wall in chemical respects because it is resistant to certain chemicals and fungi, whereas the secondary wall can be dissolved by them. The elementary fibrils are orientated in a flat spiral to the cell axis. Here, however, there are distinct differences between the species ; for example, *Pinus* has flat spirals whereas *Picea* has steeper ones.

Many species show the so-called wart-like structure in addition to the tertiary wall. This wart-like structure appears to consist of single warts and sometimes also a special homogeneous layer. The size of warts is, in most cases, submicroscopic but many differences have been found in the size, shape and density (Fig. 7, 8 & 9).

Several species, like *Picea*, *Larix*, *Pseudotsuga* and *Taxus*, do not have any warts or have only very insignificant ones. Investigations on nearly 200 soft and hardwood species have shown that there exists a close correlation between the appearance of the wart like structure and the systematic organization of these species. However, it is not possible to use the wart-like strucure for diagnosing the species.
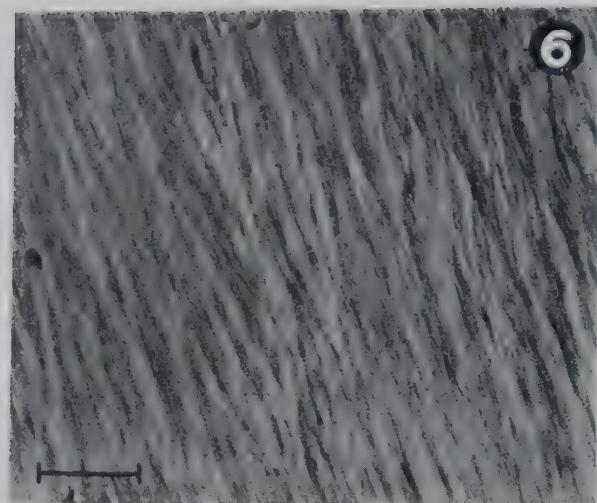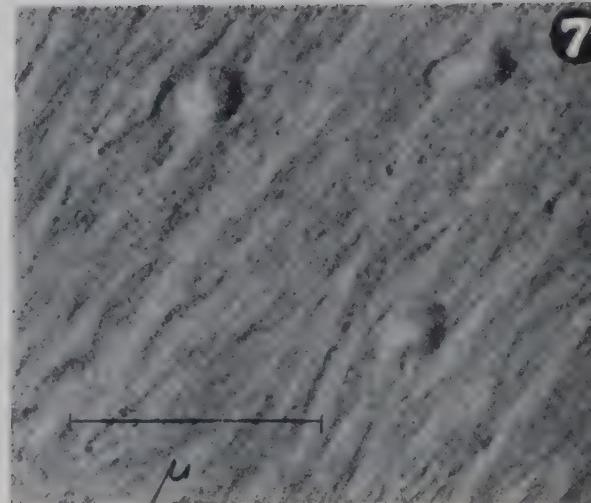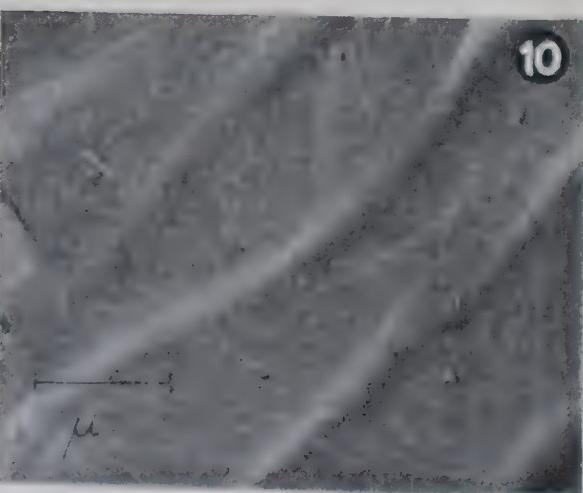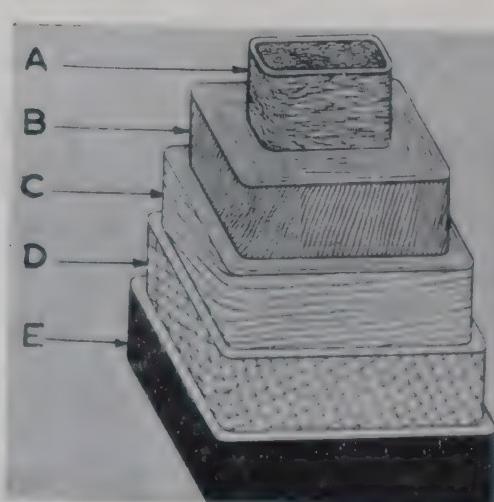
Fig. 6-11. 6—Texture of the tertiary wall of *Picea abies* (×9,900); 7—Structure of the tertiary wall of *Pinus patula* (×26,000); 8—Structure of the tertiary wall of *Widdringtonia dracomontana* (×11,900); 9—Structure of the tertiary wall of *Dendrocalamus asper* (×18,000); 10—Spiral thickenings of the tertiary wall of *Pseudotsuga taxifolia* (×2,800); 11—Model of the cell wall structure of a tracheid [A, Tertiary wall, sometimes with wart-like structure; B, Central layer of the secondary wall; C, Outer layer of the secondary wall; D, Primary wall; E, Middle lamella]

On the tertiary wall of several genera also there are spiral thickenings which can be seen by a light microscope. The spiral thickenings consist of elementary fibrils nearly arranged in parallel. The fibrils in the spirals are normally oriented differently from the fibrils of the tertiary wall below (Fig. 10). The incidence of wart-like structure and spiral thickening almost exclude each other. Besides the fine structure of the cell wall, the fine structure of the pits and the connections between the cells are also quite interesting. Its structure however cannot be described in detail here.

Fig. 11 shows the structure of lignified cell wall as seen by the electron microscope.

It should be noted, however, that the electron microscopic method of investigation demands a very good knowledge of the light microscopic structure of the object. In order to get good results it is also necessary to work thoroughly for a considerable time in this field to improve the preparation technique and more so to get experience in interpreting the results. The danger of making mistakes in preparation and examination of artefacts is great. But, by means of a proper treatment and careful interpretation we are sure to find many new and interesting facts about the structure of wood, which are also of much importance for its utilization, especially in seasoning, preservation, pulping, gluing and timber mechanics.

Gelation Behaviour of Viscose Solution and its Relation to Filterability and Fibre Properties

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Investigations carried out so far on the anomalous behaviour of viscose in solvent electrolytes and the relation between gelation and filterability and fibre properties of viscose have been reviewed. The paper describes a viscose rayon pilot plant which has been designed, fabricated and set up at the *Shri Ram Institute for Industrial Research* with the object of evolving a standard procedure for study of viscose solutions so that the procedure may be applied on an industrial scale.

Characteristics of polyelectrolytes

High polymers containing charged groups, known as Polyelectrolytes have been extensively studied[1,2] on account of their anomalous behaviour.

The most marked anomalous behaviour is in respect of viscosity in dilute solution. Thus the straight line relationship between reduced viscosity and concentration (Martin equation), normally observed with high polymers, does not hold good in their case in very dilute solutions (less than 0.1 per cent). The reduced viscosity, on the other hand, increases sharply with decreasing concentration.

The magnitude of the deviation is affected by the introduction of solvent electrolytes, which cause a change in the configuration of the polymer molecule. The ionized groups along the polymer molecular chain repel one another, thus causing the chain to straighten out. With the introduction of the solvent electrolyte, the repulsion between neighbouring ionized groups along the chain becomes less due to the screening action of the electrolyte, as a result of which the chains are allowed to coil up into a more random configuration. A change in solvation of the molecule may also occur and contribute to this effect to a limited extent.

Viscose solution as polyelectrolyte

Tait et al.[3] have studied the viscosity behaviour of commercial viscose solutions in the dilute solution range. The results, shown graphically in Fig. 1, indicate that the anomalous behaviour occurs below 0.1 per cent concentration when water is used as the diluent and that there is no such behaviour when 1 per cent sodium chloride solution is used as the diluent, although the reduced viscosity drops to a lower level. The behaviour is similar when 6 per cent sodium hydroxide solution is used as diluent, the drop in viscosity being much more marked.

However, as the authors point out, the procedure of diluting viscose with water involves a change not only in polymer concentration, but also in the concentration of solvent electrolyte.

For studying the effect of change in polymer concentration alone, the authors used a specially purified sample of sodium carboxymethylcellulose (NaCMC) having about the same molecular weight and degree of substitution as the xanthate, and studied its viscosity in water and 6 per cent sodium hydroxide solution. The results represented in Fig. 2 indicate that the magnitude of reduced viscosities of NaCMC in water is several times higher than that of the corresponding xanthate in water, although in 6 per cent sodium hydroxide solution the reduced viscosities are comparable, as is to be expected, with

Fig. 1

Fig. 2

Fig. 1—Relation between viscosity and concentration of dilute solution of cellulose xanthate in different solvents ; Fig. 2—Relation between viscosity and concentration of dilute solution of sodium carboxymethyl cellulose (CMC) in different solvents
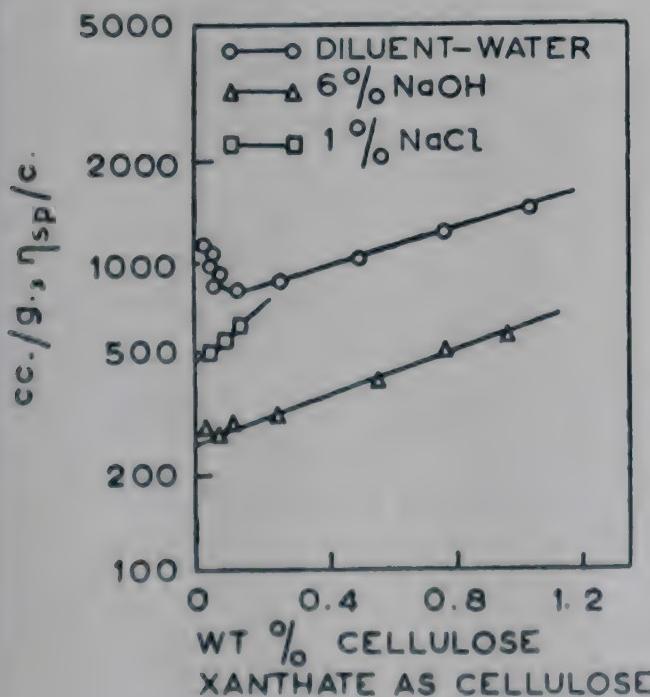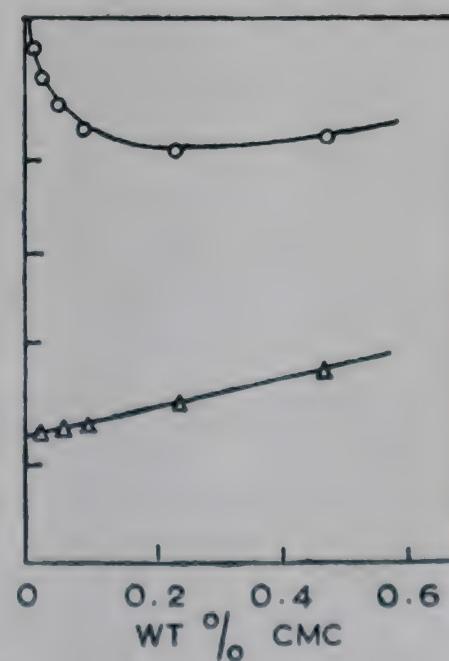
those of cellulose derivatives of the same molecular weight, if the poly-electrolyte effect is eliminated.

Quantitative estimates of the change in molecular configuration of poly-electrolytes due to added solvent electrolyte have been obtained by light scattering measurements on xanthate solutions by the above authors.

Thus it appears that cellulose xanthate in pure water, would show an even more marked change in reduced viscosity with solvent than viscose in water. It has been estimated that the intrinsic viscosity (and hence effective volume) of cellulose xanthate in pure water is 20-25 times higher than that in 6 per cent sodium hydroxide solution.

The marked difference between the effect of simple electrolytes and hydroxides on the intrinsic viscosity of viscose is believed to be due to the inter-action between the hydroxyl ions of the solvents and the hydroxyl groups in the cellulose chains.

The interpretation of the behaviour of cellulose xanthate in dilute solution has helped to explain some effects observed in relatively concentrated solutions, such as the effect of sodium hydroxide content on viscosity of viscose. It is found that with increasing alkali concentration, the viscosity goes through a minimum and rises again. The initial drop is explained as being due to the effect of sodium hydroxide in decreasing the effective volume of xanthate (as indicated by intrinsic viscosity data). The subsequent rise is due to the change in solvent powers of sodium hydroxide, which becomes a poorer solvent at higher concentration. This is shown by the increase in K (Martin equation) with increasing alkali concentration. In poorer solvents, the interference between polymer molecules becomes greater.

The study may be extended by using purified xanthate solutions freed from by-products, like sodium di- and trithiocarbonates, carbonyl sulphide, sodium sulphide and sodium carbonate, some of which are formed during xanthation, and are present in commercial solutions. The role played by these constituents has not been considered in the above study. Also, the effect of these constituents on filterability and fibre spinning properties may be studied by comparing the behaviour of purified and normal viscose solutions. Some preliminary studies on the effect of by-products on viscosities and ripening have been carried out by Heuser and Schuster[4].

The isolation of pure xanthate itself is a big problem and precipitations with alcohol, acetone, or brine[5] dialysis, ultrafiltration[6] have been tried mainly for determining the ratios of sulphur to cellulose in the purified product. A more recent technique developed by Samuelson[7] is the use of

anion exchange resins which adsorb the low molecular weight by-products efficiently.

Gelation and filterability

Viscose filterability is affected by at least two factors, namely (i) undissolved fibres, dirt, etc. and (ii) rheological factors, such as viscosity and gelation[9-10].

Bergek and Ouchterlony[10] studied the viscosity of viscose solutions under a wide range of pressures, and its relation to filter clogging. They point out that cellulose xanthate in a technical grade of viscose appears partly as primary particles, i.e. molecules or micelles, and partly as secondary aggregates, the latter partly contributing to filter clogging. The effect of pressure on viscosity is due partly to the non-spherical shape of the primary particles and partly due to the fact that the aggregated secondary particles are held together by forces smaller than the maximum flow stresses occurring under viscosity measurements, and certainly smaller than the stresses in the capillaries of spinnerettes. According to them, the secondary aggregates are broken up during pressure filtration and reaggregate after passing the filter.

Conner and Donnelly[11] investigated the state of aggregation of commercial viscose solutions using the flow birefringence technique, and found that there is no change in birefringence as a result of filtration. Thus the molecular aggregation would seem to be unchanged by filtration, but a more likely explanation is that reaggregation takes place during the period the solution stands after filtration.

Another important observation made by them is that the relaxation time, which gives a measure of the size of the aggregates, is constant and is not affected by the various sources of cellulose used and process variables. They conclude that the number, but not the size of the aggregates, is changed by the various process variables.

This observation seems to rule out the simultaneous existence of primary particles and secondary aggregates in viscose, as was concluded by Bergek and Ouchterlony. Thus it appears that there is no certainty regarding the state of aggregation of viscose, and the effect of process variables on it.

Yield point measurements[12] are a fruitful means of studying the sol-gel transition systems, where the yield point rises continuously from zero to higher values. The shearing tension to which a system will yield depends not only upon the character of the junction points, but also upon their number per unit volume. Even junction points of relatively high strength might be disrupted by a relatively small flow gradient imposed on the liquid if their number per unit volume is small. Below the gelling temperatures of

more concentrated solutions, the liquid appearance of the system is maintained and using very sensitive means, it is possible to examine yield points in such systems. Michaud[13] has described a simple apparatus for the purpose. A study of viscose solutions by this technique should give useful information, since the yield point is a function of the strength and number of junction points of a gel system, and these have an important bearing on the filterability and fibre properties.

Gelation and fibre properties

Apart from empirical studies, the correlation of gelation of viscose solution to fibre properties has been attempted in two broad directions:

(i) Study of mechanical properties of isotropic xanthate gel filaments in their various states of swelling as a function of process variables which influence the gel structure of viscose. Isotropic filaments suffer practically no strain. As such, they are merely gelatinized viscose formed into threads. The swollen filaments are xanthate filaments of almost the same xanthate ratio as viscose at the moment of spinning. These filaments are produced by the gelatinization of viscose and the filaments consequently are models of the primary gel. This work is mainly due to Hermans[14] and his collaborators.

(ii) Study of the mechanical properties of rayons and, in particular, a study of their fine structure, as a function of various degrees of ripening. The fine structure of rayons by microscopic examination of suitably swollen and dyed fibres has been studied by Schramek and Stenzel[15]. The fibres disintegrating slowly under the influence of the swelling medium, lay bare the fine fibril structure which can be observed by a suitable dyeing technique.

Viscose pilot plant

From the foregoing it is clear that there is need for suitable equipment for preparing viscose solutions according to a standard procedure so that it is possible to obtain reproducible results. With this end in view, a viscose preparation and spinning pilot plant of one kg. pulp capacity per batch has been designed, fabricated and erected at the *Shri Ram Institute for Industrial Research*. This capacity was chosen after taking into consideration similar plants in research institutes like *Pulp and Paper Research Institute*[16], Norway, the research section of *American Viscose Corporation*[17] as well as German standard specifications for viscose preparation, filterability determination, etc.

A description of the various units of the pilot plant has been published[18]. Work on increasing the spinning capacity to 5-6 spinneret positions, provision of coagulating bath, and on the circulation and filtration systems is in

progress. A few viscose preparations and spinning trials have been made and work on standardization of various operations is being continued.

SUMMARY

In spite of the large amount of work that has been and is being done on the gelation of viscose solutions, there appears to be no certainty regarding the state of aggregation of particles in solution and its correlation to filterability and fibre properties. Some directions in which further work may be continued are indicated. Details of the viscose pilot plant set up at the *Shri Ram Institute for Industrial Research* for enabling further investigations on the behaviour of viscose solutions have been given.

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Effect of Cellulose Structure on Tensile Properties of Cotton

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Literature on structural differences of cellulose contained in various types of cottons, their methods of determination and their effect on tensile properties of cotton has been reviewed. The results obtained in support of existence of a correlation between tensile strength and degree of fibrillar orientation and degree of polymerization of cotton are presented.

It is well known that cotton fibre is one of the purest forms of naturally occurring cellulose and that it consists of a large number of cellulose molecular chains. Although all types of cotton fibres are chemically the same, still large variations are observed in their physical properties depending on the variety of cotton. Some of the factors that contribute to this variability are due to structural differences, such as degree of crystallinity of cellulose, degree of orientation of cellulose crystallites with respect to fibre axis, and mean chain length or mean degree of polymerization of cellulose molecules.

Degree of crystallinity

At certain regions along the length of the cellulose fibres, the molecules are well arranged in a three dimensional order. These regions are referred to us crystalline regions. At other regions, the arrangement of the molecules is less orderly. Both physical (X-ray, density, etc.) and chemical (acid hydrolysis, iodine adsorption, etc.) methods have been used to estimate the amount of crystalline regions in the fibres. The physical methods are used to measure the actual percentage of crystallinity and the chemical methods, to measure the amount of amorphous or accessible regions. Since the arrangement of molecules in a part of the non-crystalline region is of a higher order than in the strictly amorphous regions, the chemical methods do not measure the total amount of non-crystalline regions. Results of X-ray and optical (birefringence) methods of estimating the crystallinity of cellulose have shown that the degrees of crystallinity of some naturally occurring fibres, namely cotton, flax, and ramie, are the same[1]. Hence, the chances of differences in the degree of crystallinity of cellulose fibres

belonging to different cotton varieties are negligible. Moreover, Bhujang and Nanjundayya[2] have shown that the degree of accessibility of different cottons is the same. Hence it can be concluded that the differences of physical properties of cotton fibres are not due to any difference in the degree of crystallinity of the cellulose fibres.

Degree of fibrillar orientation

The arrangement of the molecular chains in the crystalline regions of the fibre with respect to the fibre axis is referred to as fibrillar orientation. It has been observed that the degree of fibrillar orientation varies from one group of naturally occurring cellulose fibres to another and also from one variety to another in the same group of cellulose fibre. A brief survey of literature on the measurement of fibrillar orientation and the effect of orientation on tensile properties is presented below.

Measurement of orientation

The degree of orientation of cellulose crystallites with respect to the fibre axis can be measured either by optical or X-ray diffraction methods[5], the latter being more commonly employed for this purpose.

(i) *Optical methods* —The optical methods are based on the phenomenon of polarized fluorescence or dichroism or birefringence. In the first method, the fibres are dyed with certain dyes and the percentage of polarization of the fluorescent light is measured. From this, the arrangement of the dye molecules, and hence the orientation of the micelles, is obtained[3].

The phenomenon of dichroism was first used by Preston[4] for measuring orientation. In this method, the fibre is dyed with a direct dye and the absorption of light by the dyed fibre is measured both when the plane of polarization of incident light is parallel and when the plane of polarization is perpendicular to the fibre axis. A similar method was employed by Morey[5] in his later investigation using a bundle of fibres.

Hermans[6] and Meredith[7] have measured the degree of orientation by measuring the double refraction of fibres. The refractive indices of the fibres are measured when the plane of polarization of incident light is (i) parallel to the fibre axis and (ii) the plane of polarization is perpendicular to the fibre axis. The difference in the two refractive indices has been used as a measure of orientation by Meredith whereas, the optical orientation factor (which is the ratio of double refraction of the fibre to that of an 'ideal' fibre) has been used by Hermans.

(ii) *X-Ray methods* The procedure generally adopted in these methods is to obtain a diffraction pattern by passing a beam of X-rays through a

specially prepared bundle of parallel fibres held vertically in the path of
the X-ray and then measuring the distribution of intensity along the 002
diffraction arcs in the X-ray photographs.

Sisson and Clark[8] who first used this method assumed that the distribution
of crystallites around the region of the fibre bundle through which the X-ray
beam is passed is proportional to the distribution of intensity around the
002 diffraction ring. The observed intensity values were converted into
percentage values and these were then expressed as distribution curves.
The curves were observed to be similar to normal curves. The orientation
calculated by different statistical methods was expressed as the angular dis-
tance from the point of maximum density to the points of the median, the
mean and the standard deviation of density. Later, Sisson[9] observed that
the angle between the point of maximum blackening on the 002 diffraction
arc and that on the arc at which the density is 40 per cent of the maximum
could be taken as a measure of orientation. This angle is commonly referred
to as the 40 per cent X-ray angle. Berkley and coworkers[10-14] have also
used the 40 per cent X-ray angle as a measure of orientation and have given
a detailed procedure for measuring it for different varieties of cotton.

Other methods of evaluating the degree of fibrillar orientation from X-ray
diagrams of cellulose fibres have been given by Go and Kubo[15], Hermans
et al.[16] and Tsien[17]. Go and Kubo calculated the degree of orientation by
means of a formula using the value of width of the intensity curve at half
of the maximum intensity of the strongest equatorial interference (002
diffraction arc in the case of natural cellulose fibres). Tsien assumed that
the number of crystallites included in any angular interval is a function of
the angle to the fibre axis and based on this asumption, devised a method
by which the angular distribution curve of crystallites around the fibre axis
could be obtained by analysis into its components of the equatorial inten-
sity of the 002 diffraction spot. A better method of evaluating the orienta-
tion is due to Hermans et al. who have theoretically shown, in the case of
regenerated cellulose fibres, that the degree of orientation, expressed as the
orientation factor f_x, can be calculated from the measurement of the dis-
tribution of intensity along the 10$\bar{1}$ and 002 diffraction arcs. They have
shown that the orientation factor f_x is very nearly equal to the orientation
factor f_o, calculated from measurements of birefringence.

Meredith[18] has used three measures for the degree of orientation, namely
(i) 40 per cent X-ray angle (absorption), (ii) 40 per cent X-ray angle (in-
tensity), and (iii) orientation factor. The procedure followed by Meredith
for measuring the 40 per cent X-ray angle (absorption) is similar to that of
Berkley and coworkers. He also obtained a calibration strip on the X-ray
film by making six exposures which increased by a factor of two at each
step : from this, he obtained a calibration curve for X-ray intensity.

Employing this calibration curve, the X-ray intensities at the positions of maximum and minimum blackening were calculated and 40 per cent of difference was added to the minimum value. From the calibration curve, the intensity of light transmitted corresponding to this X-ray intensity was calculated and used to determine the 40 per cent X-ray angle (intensity) from the micro-photometer record of 002 arc. For the measurement of the orientation factor, Meredith had made use of the relation derived by Hermans et al.[16] in the case of viscose fibres. From the intensity distribution along the 002 arc the orientation factor (f) is obtained from the relation

$$f \, \Omega \, 1 - 3 \, \overline{\sin^2 a}$$

$$\text{where } \overline{\sin^2 a} = \frac{\int_0^{\pi/2} I \sin^2 a \, \cos a \, da}{\int_0^{\pi/2} I \cos a \, da}$$

and I = intensity at an angle a measured from the equator. The integrals were evaluated by plotting graphs of $I \sin^2 a \, \cos a$ versus a and of $I \cos a$ versus a and then measuring the area under these curves.

As can be seen from the above, measurement of the orientation factor involves laborious calculations. Hence the 40 per cent X-ray angle is taken as the measure of orientation generally. Some investigators, especially those[19] using a Geiger counter diffractometer for measuring the X-ray diffraction intensities, however, use another parameter called the 50 per cent or half maximum X-ray angle which can be defined in the same manner as the 40 per cent angle. Although the choice of the 40 per cent angle is purely arbitrary, it is interesting to note that recently Stern and Stout[20] have shown that the 40 per cent X-ray angle is, on the average, a good approximation to the root mean square value of the spiral angle. Hence, the author has used in his investigation[21] the 40 per cent X-ray angle as a measure of the fibrillar orientation.

Effect of Orientation on Tensile Properties

Clark et al.[22] were the first to observe that three varieties of cotton which differed in their X-ray patterns also showed different physical properties. Sisson and Clark[8] showed the existence of some relationship between the tensile strength and degree of fibrillar orientation of cotton fibre by measuring the distribution of intensity along the 002 diffraction arc.

Morey[23] studied the relation between orientation of fibrils determined by the optical method and tensile properties of cellulose fibres. Although he did not get very satisfactory results with cotton fibres, he observed that in the case of rayons, the orientation had a definite effect on tensile strength, the better oriented fibres showing higher strength. Later, Sisson[7] derived the relationship between the 40 per cent X-ray angle and the Chandler bundle strength by making measurements on four varieties of cotton. Using this

relation, he predicted the Chandler bundle strength of six varieties of cotton. The predicted value of the bundle strength showed a correlation coefficient of 0.97 with the actual values of strength. Similarly he observed the correlation coefficient between the actual and the predicted values of strength to be 0.867 in the case of another set of 21 varieties of cotton. It is to be noted that as the X-ray angle increases, the tensile strength generally decreases.

Berkley and Woodyard[10] have directly correlated the X-ray angle and the bundle strength in the case of 30 varieties of cotton and observed a correlation coefficient of −0.951 between the X-ray angle and the Chandler bundle strength. Hessler et al.[14] used the Pressley strength index at nominal zero gauge instead of the Chandler bundle strength, and found a correlation coefficient of −0.75 between the Pressley strength and X-ray angle in the case of 42 varieties of cotton.

A more detailed investigation of the relation between X-ray angle and the Pressley strength was carried out by Berkley and Barker[13]. They observed that a higher correlation between X-ray angle and fibre strength could be obtained if the different varieties of cotton were grouped according to the botanical species to which they belong. Meredith[24] has also stated that when the values of tensile strength are plotted against those of X-ray angles, the points fall ino definite groups according to the botanical species to which the cotton samples belong.

Meredith[24] has further observed that the X-ray orientation factor gave a slightly higher correlation with strength than the 40 per cent X-ray angle. He, moreover, showed experimentally that there is a close correlation between the X-ray angle and the convolution angle of the cotton fibre. In an earlier investigation[7] he had observed close correlation between tensile strength and Young's modulus of cotton and orientation measured by double refraction. Recently Hertel and Craven[25] have observed a correlation between fibre bundle elongation (as measured by the Stelometer) and the X-ray angle. The relationship between X-ray angle and a number of fibre properties has been investigated by Rebenfeld and Virgin[26] who have observed significant correlations between X-ray angle and the following fibre properties: (i) Pressley bundle strength at 0 mm. and 1.5 mm. gauges, (ii) count-strength product of 36s yarn, (iii) fibre breaking stress, (iv) fibre elastic modulus, and (v) fibre breaking elongation.

From the above survey of literature it can be seen that the tensile properties of cotton fibre are very closely related to the degree of fibrillar orientation. The author has recently studied[21] the relationship between X-ray angle and tensile strength in the case of 33 varieties of cotton and observed that the X-ray angle gave a higher correlation (−0.67) with Pressley strength index

at zero gauge than (– 0.46) with the breaking strength measured on individual fibres. A similar observation has been made by Rebenfeld and Virgin[26] who have further observed that Pressley strength at higher gauge lengths gave a lower correlation with X-ray angle. These differences have been explained by them on the ideas put forward by Wakeham and Spicer[27] regarding the existence of weak points along the length of the cotton fibre. While testing individual fibres or fibre bundles at higher gauge lengths, the test lengths being larger than in the case of bundles tested at zero gauge lengths, the weak points of the fibre come into prominence and hence the strength of the fibre is decided by the strength at the weak points. This causes lowering of the correlation value.

Subsequent results obtained by the author have also confirmed the conclusion that there is great degree of correlation between the X-ray angle and the Pressley strength index measured at zero gauge length. Till now investigations have been confined only to those varieties of cotton belonging to the pure line botanical species. With a view to testing whether this relation is observed in the case of cottons evolved by crossing two different botanical species, ten strains belonging to an Indo-American inter-species cross were investigated[28] and a correlation coefficient of – 0.93 was observed between the X-ray angle and the Pressley strength index. This value is significantly higher than that (– 0.67) observed by the author in his previous investigation on 33 varieties of cotton, probably because in this case all the ten varieties of cotton belonged to the same group although of an inter-species cross, whereas in the other case the cottons belonged to different species. More recently a correlation of – 0.925 has been observed between X-ray angle and the Pressley strength index (measured at nominal 0 in. gauge) of nine samples of cotton, all belonging to the *Hirsutum* species, grown under the Rice Fallows Scheme in Madras State. These results support the view of Meredith[24] and Berkley and Barker[13] that it would be better to group the cottons according to the botanical species to which they belong for purposes of correlating X-ray angle with tensile strength.

From the above results it can be concluded that the tensile strength of cotton is related to a very great extent to the degree of fibrillar orientation of cellulose crystallites in the fibre. In the case of cotton belonging to the same botanical species, the X-ray angle of a cotton is a very good measure of its tensile strength. Further work on the relation between X-ray angle and other properties of cottons (e.g., rigidity, tensile strength at different gauge lengths, etc.) is under progress.

DEGREE OF POLYMERIZATION

A sample of a high polymer substance, such as cellulose, generally consists of molecules of different sizes and different degrees of polymerization (D.P.).

Hence the various methods used for measuring D.P. of a high polymer sample give only an average D.P. of all the molecules constituting the sample. Of the various methods commonly used for the determination of D.P., some (e.g., light scattering, ultracentrifuge) give the weight average D.P. value while the method based on the measurement of viscosity of a high polymer solution gives a value which is different from the number average and weight average values, although in most cases it is nearer the weight average value.

Determination of D.P.

Most of the methods mentioned above have been used for determining the D.P. of cellulose either in the pure state or as acetate or nitrate. The most commonly used method is the one based on the measurement of viscosity of solutions in suitable solvents. The viscosities of solutions of different concentrations are measured and from these values, the intrinsic viscosity is calculated. From the value of intrinsic viscosity, the D.P. is determined by the Staudinger relation[29] as modified by Mark[30] and Houwink[31].

To enable the viscosity method to be used as a rapid method for measuring D.P. in routine work, Battista[32] has given an empirical equation for deriving the approximate D.P. from viscosity determinations carried out at a single concentration.

In the present work, the standard British Cotton Industry Research Association method[33] has been employed for measuring the viscosity of 0.5 per cent solutions of different cottons in cuprammonium hydroxide and, using Battista's relation, the values of D.P. of cellulose in the cottons have been determined from viscosity values. Although Battista's relation gives only an approximate value of D.P., it can be used for obtaining comparative values of D.P. of different cellulose samples.

Effect of D.P. on physical properties

Earlier work on the relation between D.P. and mechanical properties was mainly concerned with the loss in strength of natural fibres brought about by chemical degradation ; later work was concerned with the relation between D.P. and mechanical properties of regenerated fibres.

As early as 1926, Birtwell, Clibbens and Geake[34] observed that the loss in strength of cotton fibres brought about by acid hydrolysis was accompanied by a fall in cuprammonium viscosity. Ridge and Bowden[35] observed a similar effect in the case of regenerated cellulose fibres.

Later, Staudinger et al.[36] carried out a systematic study of the relation between mechanical properties and D.P. by treating cotton and ramie fibres

with acids to form a homologous series of cellulose fibres. They observed that the tensile strength increased rapidly as D.P. increased from 200 to 700 and slowly thereafter. The results showed that regenerated cellulose fibre had a higher strength than degraded natural fibre of the same D.P. At about the same time, Plötze and Person[37] reported that the X-ray data of ramie and cotton fibres were not affected by degradation of the fibre.

Mark[38] has summarized the early work and drawn some generalizations therefrom. Broadly it has been shown that a minimum value of D.P. is necessary for developing mechanical strength ; from this minimum value, up to a value of about 250, the strength increases rapidly with D.P. beyond which it increases only slowly. These generalizations were confirmed by Sookne and Harris[39] who prepared films of fractionated cellulose acetate and measured their tensile strength and D.P. Their results showed that tensile strength depends only on the number average D.P. value and that in the case of a blend, the strength is equal to the weight average of the strengths of individual components forming the blend. These results lead to the conclusion that tensile strength should be a linear function of the reciprocal of the number average D.P. value[40].

It may be seen from the foregoing that tensile strength is not proportional to D.P. However, Hessler et al.[14] have recently shown that the tensile strength of cotton is dependent on D.P. even in the range 8,000-10,000 ; cottons with higher D.P. showing better strength. The correlation coefficient between D.P. and strength was found to be 0.74 in the case of 40 varieties of cotton studied by them. They observed also that the correlation coefficient of X-ray angle and tensile strength had a value of 0.70, and when the strength was correlated with X-ray angle and D.P. together, the value of the multiple correlation was 0.84, which was higher than the individual correlation coefficients.

Recently the author has measured the D.P. of nine varieties of cotton using Battista's relation and has observed a significant correlation coefficient of 0.71 between D.P. and the Pressley strength index (at 0 in. gauge). This correlation coefficient is rather low probably because the D.P. determinations have been carried out by viscosity measurements at a single concentration. It is now proposed to confirm these results by determining the D.P. by viscosity measurement of cotton solutions in cupriethylenediamine.

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Improvement in the Spinning Quality of Jute by Chemical Modification

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The structure of jute fibre as revealed by chromatographic analysis is discussed and it is concluded that the spinning quality may be improved if some of the linkages in jute structure are broken by chemical treatment.

The spinning quality of jute, *Bimli* and *Mesta* fibres has been determined by a novel laboratory method developed earlier. Softening of jute fibre in oil-in-water emulsion, breakage of ester linkage by caustic soda treatment and combined caustic soda treatment and emulsion softening improve the spinning quality of jute fibre.

The chemical make-up of jute fibre by paper chromatographic analysis of the fractionally hydrolysed jute holocellulose and alpha-cellulose has been the subject of investigation by the author and his associates for the last few years[1-7]. Some typical results of the investigations are indicated in Fig. 1-5. From these results it may be assumed that jute fibre is made up of (*i*) long chains of alpha-cellulose consisting mainly of glucose and a small amount of xylose, arabinose and mannose (the presence of a considerable amount of galactose and a small amount of glucuronic acid has also been reported recently) ; (*ii*) medium chains of pentosans consisting of xylose and arabinose ; (*iii*) medium chains of polyuronides containing glucuronic and methyl glucuronic acids ; and (*iv*) short chains of hexosans made up of glucose, galactose, mannose and also methylpentosan, e.g. rhamnose.

All these chains run more or less parallel to the direction of fibre axis as shown in Fig. 6. In addition, the presence of lignin in sufficient quantities has to be taken into account.

Some progress has been made in recent years on the stabilization of individual chain molecules into individual jute filaments and on the nature of the linkages.
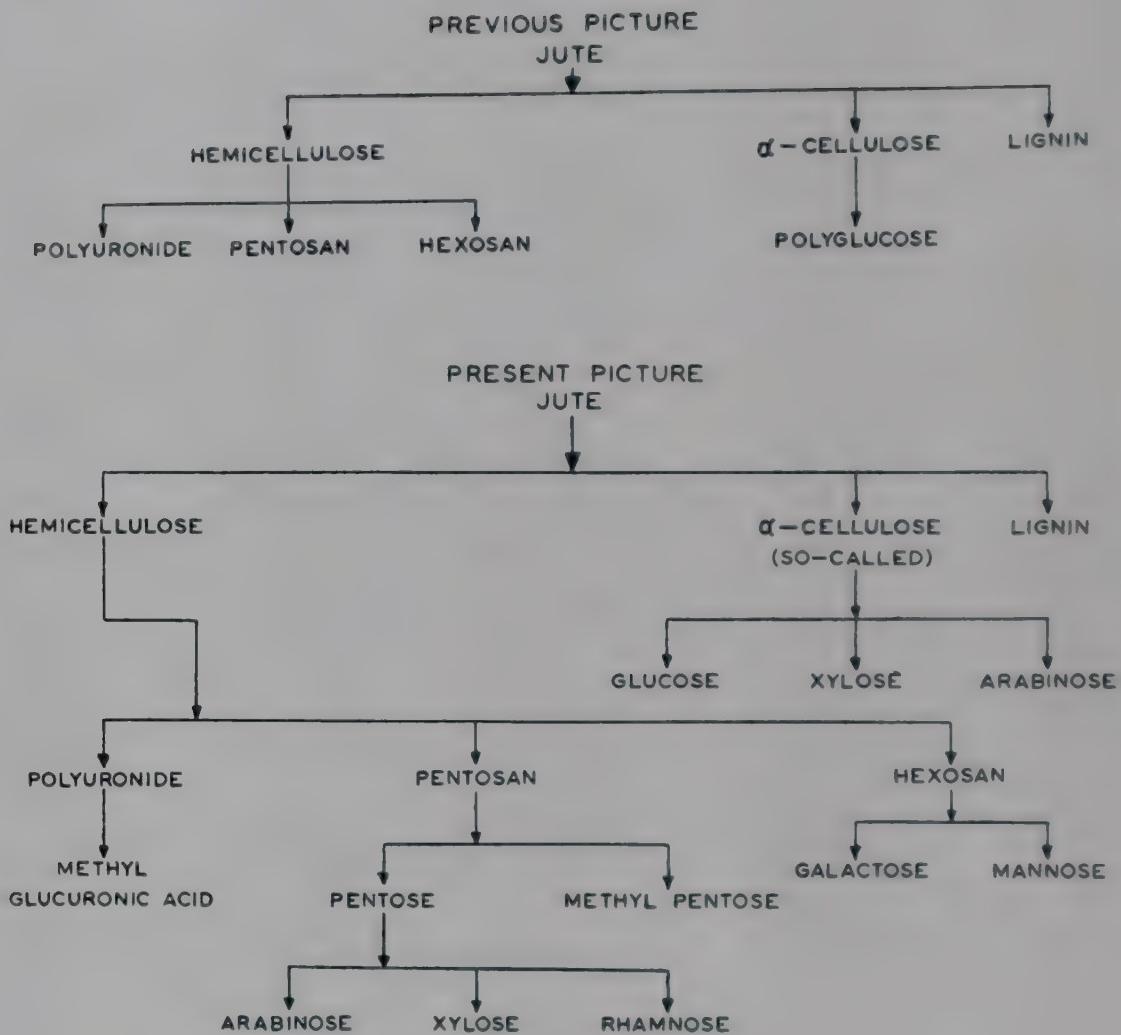
FIG. 1—CHEMICAL MAKE-UP OF JUTE FIBRE

Lignin-polyuronide linkage—Sarkar *et al.*[8] studied the total and free COOH groups in jute fibre and suggested that half the number of COOH groups occurs in ester combination with lignin hydroxyl groups. Later on, these workers and Pal[9] observed that the acid value of the holocellulose portion of jute increases during delignification by sodium chlorite and that the rate of delignification is greatly increased, if the jute fibre is pretreated with a dilute solution of caustic soda. These observations lend support to their previous assumption[8] that there is linkage between lignin and polyuronide.

Lignin-cellulose/hemicellulose linkages—Das *et al.*[10,11] postulated that the colour of raw jute is due to that part of the lignin whose enolic OH group is not engaged with other active groups of adjacent chains. In the case of white jute, however, the enolic OH groups of lignin are combined with
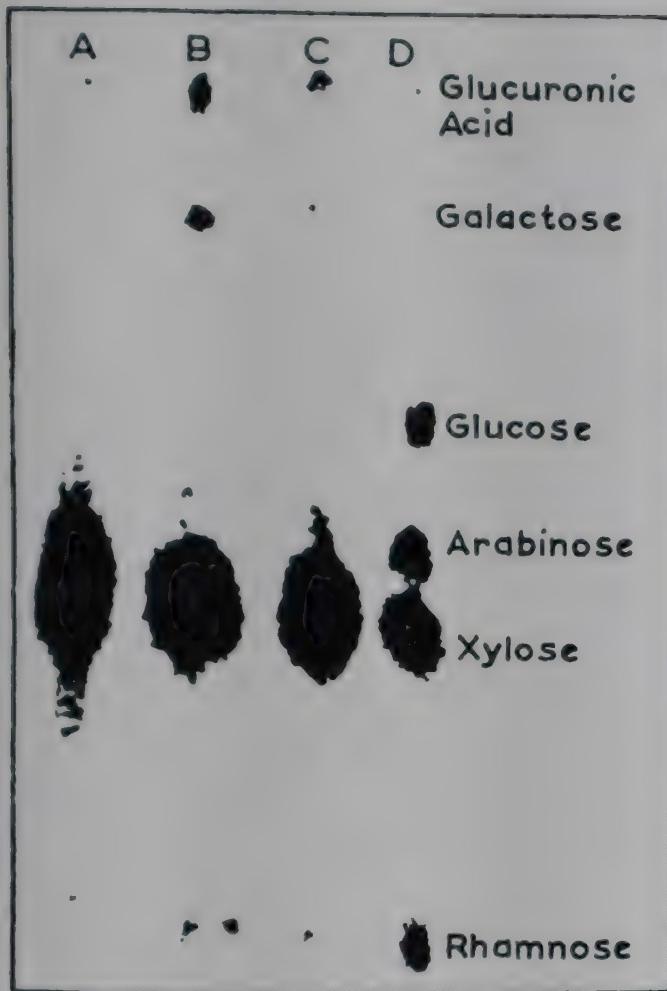
Fig. 2
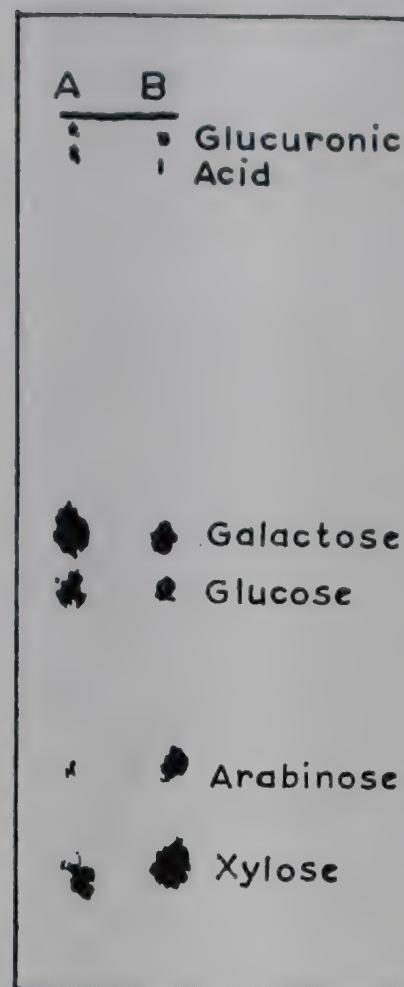
Fig. 3

FIG. 2—CHROMATOGRAM OF HOLOCELLULOSE (FRACTION 1) IN *n*-BUTANOL (7 HR)
[A, Bimli holocellulose ; B, Mesta holocellulose ; C, Jute holocellulose ; D, reference
sugars: glucuronic acid, galactose, glucose, arabinose, xylose and rhamnose] ;
FIG. 3—CHROMATOGRAM OF JUTE HOLOCELLULOSE (FRACTION 1) IN *n*-BUTANOL (168 HR)
[A, Jute holocellulose ; B, Reference sugars: glucuronic acid, galactose, glucose,
arabinose and xylose]

the active groups (OH of COOH) of the cellulose/hemicellulose chains as
illustrated below:

CASE 1

— O —   HO—| ——————————→ | — O —

Lignin   Cellulose or   Lignin-cellulose
(coloured)   hemicellulose   hemicellulose combination
                                                        (colourless)

CASE 2

O —   HOOC—   —————————→   — O — CO —

Lignin   Polyuronides   Lignin-polyuronide
(coloured)   combination
                                                        (colourless)
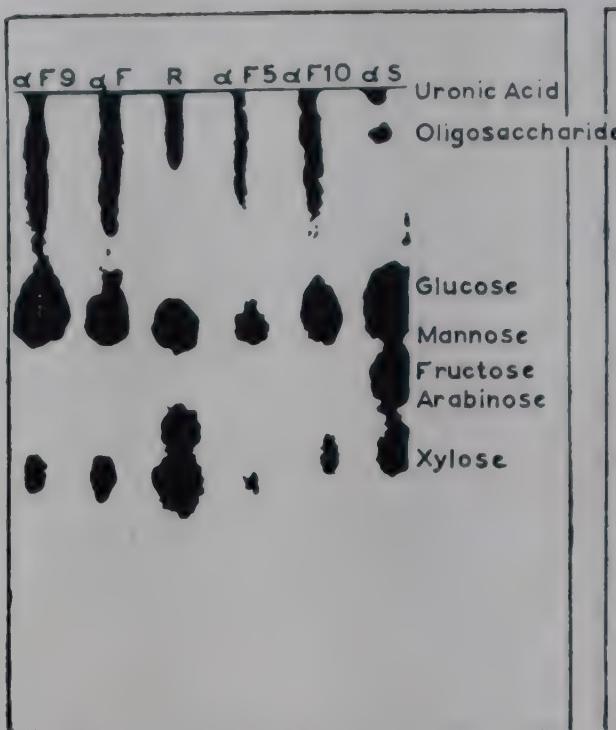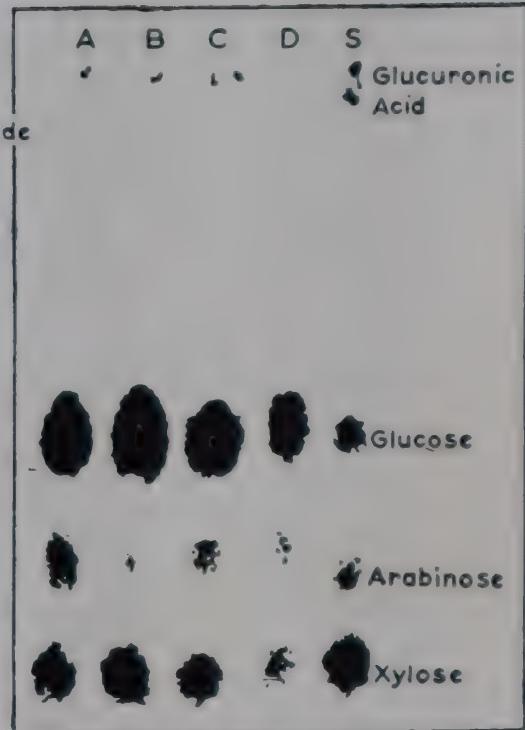
Fig. 4

Fig. 5

FIG. 4—CHROMATOGRAM IN MOIST n-BUTANOL (192 HR) [αF9—Formic acid (85%) hydrolysate of jute α-cellulose (holocellulose treated with cold 9.3% NaOH); αF—Formic acid (85%) hydrolysate of jute α-cellulose (A.C.S. treated with 17.5% NaOH); R—Reference sugars: galactouronic acid, glucose, arabinose and xylose; αF5—Formic acid (85%) hydrolysate of jute α-cellulose (holocellulose boiled with hot 5% alkali for 4 hr); αF10—Formic acid (85%) hydrolysate of jute with hot 10% alkali for 4 hr; αS—H_2SO_4 (72%) hydrolysate of jute α-cellulose (A.C.S. holocellulose treated with cold 17.5% NaOH and modified)]. The spots corresponding to arabinose and mannose for αF9, αF, αF5 and αF10 were too weak to be reproduced in the photograph; FIG. 5—CHROMATOGRAM OF α-CELLULOSE IN n-BUTANOL (108 HR) [A, α-cellulose prepared by chlorine dioxide method; B, prepared by Cross and Bevan method; C, prepared by Norman and Jenkins method; D, Reference sugars: glucuronic acid, glucose, arabinose and xylose]

This linkage has been confirmed by the detection of glucose, xylose and arabinose through chromatographic analysis of the hydrolysate of isolated lignin.

Cellulose-pentosan linkages—Several papers[3-7] on the existence of cellulose-pentosan linkage have appeared. It has been shown by chromatography that a definite association exists between cellulose and pentosan in jute alpha-cellulose. When jute alpha-cellulose is hydrolysed and the hydrolysate is chromatogrammed, glucose, xylose, arabinose and mannose can be identified. Their presence has been confirmed by the isolation and identification of a disaccharide and a trisaccharide, e.g. glucose/xylose and glucose/arabinose/xylose.

Pentosan polyuronide linkage—During the hydrolysis of jute holocellulose, an oligosaccharide[1,2] was isolated, which on further hydrolysis gave xylose
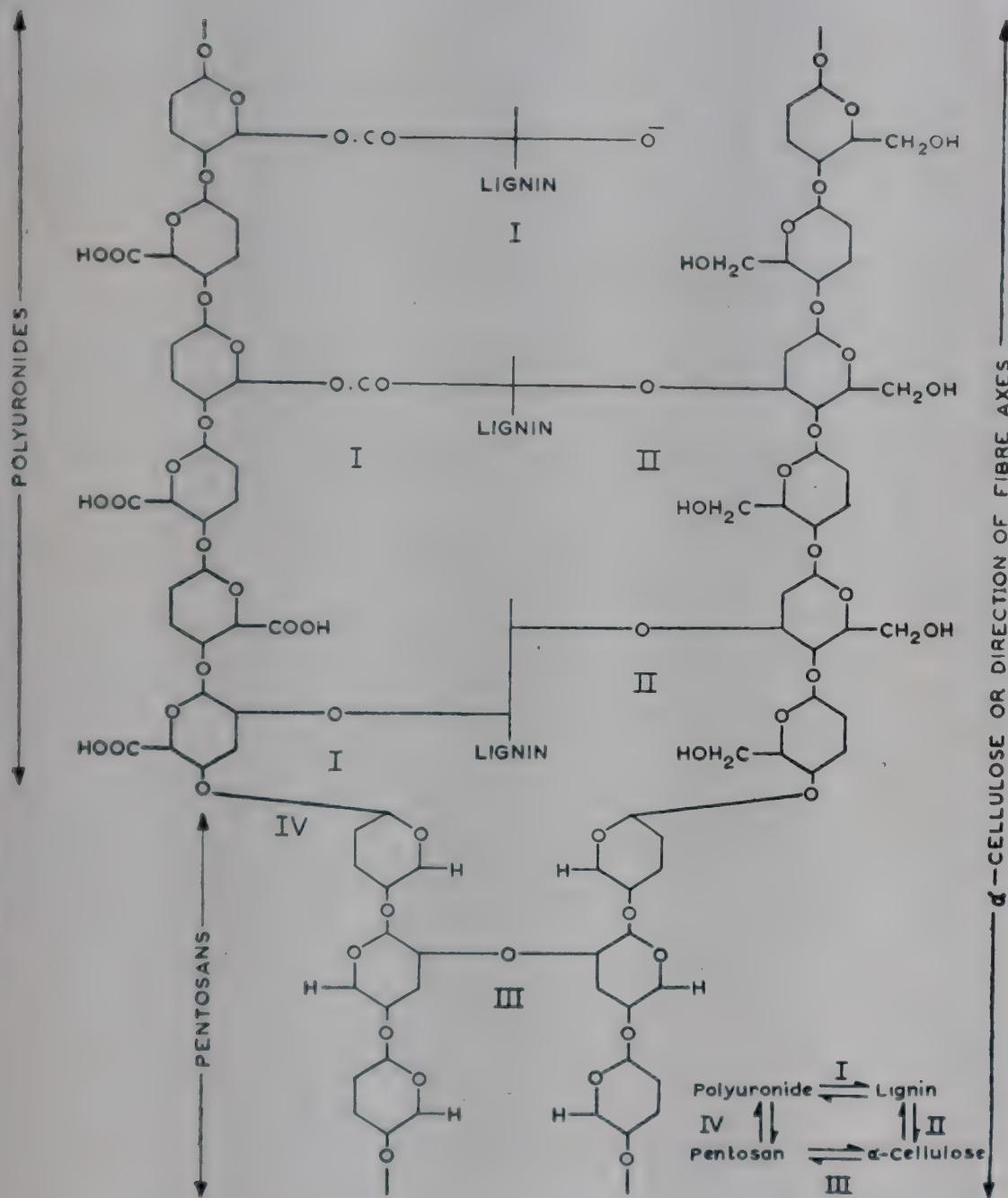
FIG. 6—ARRANGEMENT OF CELLULOSE, HEXOSANS, PENTOSANS, POLYURONDIES AND LIGNIN IN DISORGANIZED PART OF THE FIBRE

and glucuronic acid thus indicating a linkage between pentosan and polyuronide.

It has been previously suggested[12-14] that jute fibre is made up of chains of alpha-cellulose, pentosans, polyuronides and hexosans, running more or less in the direction of the fibre axis and that the chains are stabilized by innumerable hydrogen bonds and various types of linkages. Based on this concept, the author had suggested[12-14] a tentative structure of jute fibre representing more or less the non-crystalline or amorphous part of the fibre as shown in Fig. 6.

It can be seen from Fig. 6 that the rigidity of jute fibre is due to cross-linkages between running chains. It was therefore assumed that if some of these linkages are broken, the rigidity of the fibre would decrease resulting in improved spinning property. The drawback of this method is that it lowers the tensile strength of the individual fibre. However, this can be overcome by (i) selecting the right chemical for this purpose which will break down specific linkages without attacking the main chains or other linkages and (ii) by making stronger yarns with fibres of low breaking strength but of high flexibility.

It was first considered essential to find out a laboratory method for assessing the spinning quality of jute fibre before any mill trial is undertaken. Besides, in order to get precise information on the relation between the breakdown of specific linkages and the spinning quality, it is better to concentrate on a single filament. Keeping these considerations in view, a simple laboratory method of assessing the spinning quality of jute fibre was developed[16]. The method depends on the twisting of the fibre in a twist counter until the fibre breaks. Fibre quality index (F.Q.I.) is calculated by the equation. $F.Q.I. = t/m$ where t is the breaking twist (i.e., number of turns/in. required to break the fibre) and m is the mass in g./cm. length.

This method has been applied for the determination of the spinning quality of *Bimli*, *Mesta* and jute fibres. The results have been statistically analysed[17] and found to be significant at 5 per cent level (Fig. 7). *Bimli* and *Mesta* fibres possess lower spinning quality than jute.

Wet spinning—As flax spins much better in the wet condition than in the dry state, the spinning of jute in wet and dry conditions was also determined using the above method. The average of 20 individual readings of F.Q.I. values was 63.2 for wet jute and 66.5 for dry jute. This indicates that unlike flax, jute fibre does not spin better in the wet condition. This can be explained by the fact that unlike flax, jute has many cross-linkages due to the presence of lignin (Fig. 6).

Emulsion softening—The industrial success of jute processing is mainly due to the method of softening by oil-in-water emulsion. The effect of the emulsion on F.Q.I. of the fibre has been studied. The results (Table 1) are in accord with the view that the emulsion improves the spinning property of the fibre ; this property improves with increase in the oil applied, reaching a maximum at *c*. 6 per cent.

Effect of breaking ester linkage on the spinning property of fibre—It can be expected from Fig. 6 that if the ester linkages are broken, as for example with sodium hydroxide solution, the spinning property would be improved.

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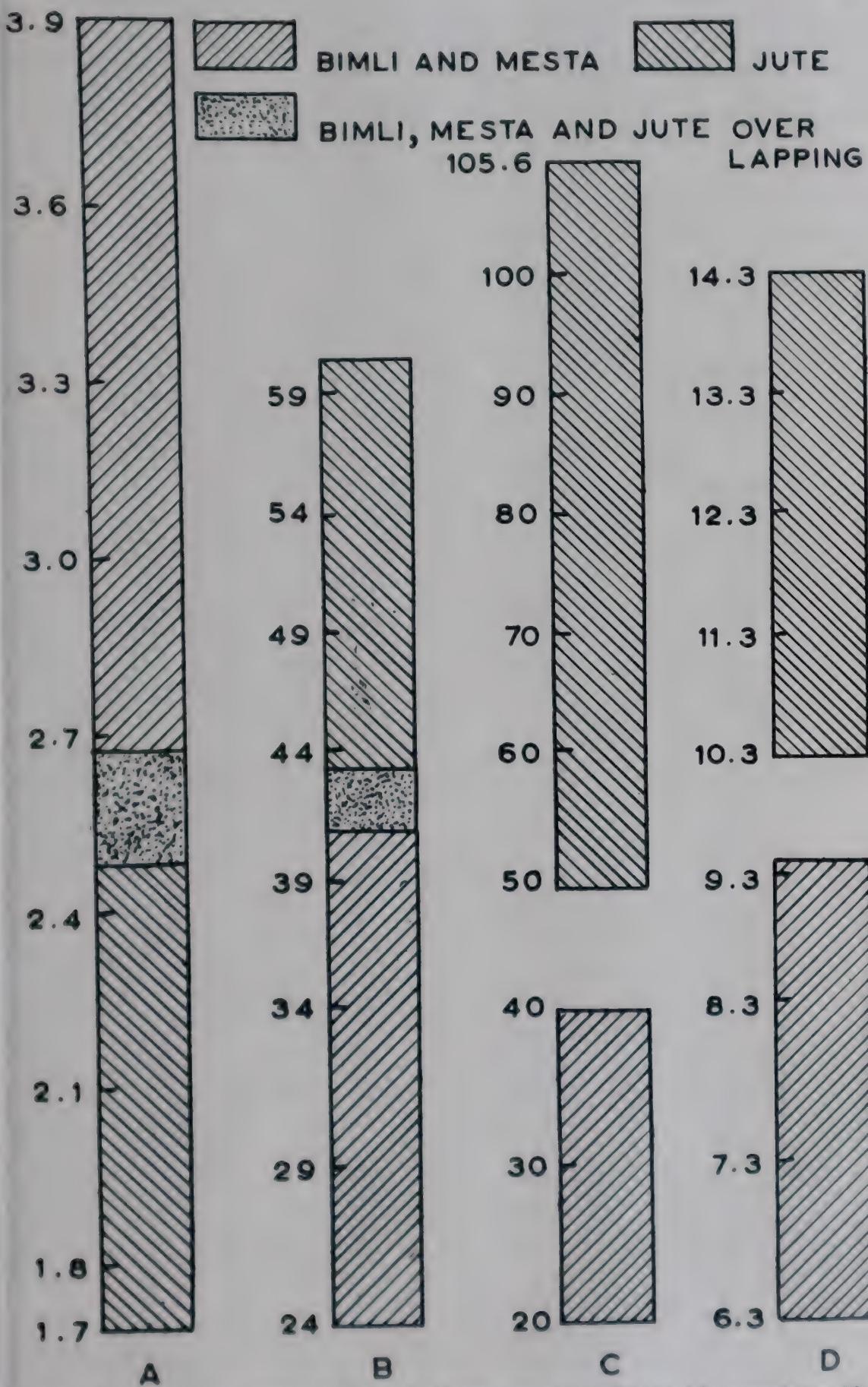
FIG. 7—CHARACTERISTICS OF BIMLI & MESTA AND JUTE FIBRES [A, mass in g. 10-4 per 3 in. length of fibre ; B, breaking twist in turns per 3 in. length ; C, F.Q.I. values ; D, lignin content (%).]

5

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TABLE 1—EFFECT OF OIL-IN-WATER EMULSION ON F.Q.I.

% OIL ON FIBRE	F.Q.I.*
0 (Untreated)	69.9 ; 68.5 ; 61.1
2	76.7 ; 79.5
4	76.5 ; 80.0
6	89.0 ; 81.4
10	82.0 ; 83.0
14	88.4 ; 80.0

* Av. of 20 individual values.

TABLE 2—EFFECT OF SODIUM HYDROXIDE ON F.Q.I.

ALKALI CONCENTRATION %	F.Q.I.*
0 (Untreated)	69.0
1	70.0
5	88.2
12.5	130.6

* Av. of 20 individual values.

TABLE 3—COMBINED EFFECT OF SODIUM HYDROXIDE & OIL-IN-WATER EMULSION ON F.Q.I.

ALKALI CONCENTRATION %	F.Q.I.*	
0	82.0 ;	83.0
1	84.2 ;	82.9
5	102.8 ;	90.9
12.5	120.0 ;	119.3

* Av. of 20 individual values.

With a view to verifying this possibility, the effect of sodium hydroxide solution on F.Q.I. of the fibre was studied. The results (Table 2) indicate that the breakdown of ester linkages results in a significant increase in F.Q.I. The breakdown of linkages takes place when the concentration of sodium hydroxide solution is 5 per cent or more.

Effect of emulsion on the spinning property of alkali-treated fibre—The alkali-treated fibre was treated with oil-in-water emulsion to give 10 per cent oil content on the fibre and the F.Q.I. values were determined. The results

(Table 3) indicate that the treatment increases the spinning property considerably. Alkali of low concentration (1 per cent) has no significant effect on F.Q.I.

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Crease Resistance of Cellulosic Textiles in Relation to Fabric Geometry

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One of the desirable properties in a fabric is its ability to recover from crease imposed in service. It is well known that the combination of desirable properties found in natural fibres in general, and cotton in particular, is yet unmatched by artificial and synthetic fibres. In view of the important position occupied by cotton in India's national economy, it is necessary that maximum advantage is made of its properties.

Poor recovery in cotton fabrics

However, it is particularly the cotton garments that show poor crease recovery ; a few days' wear imparts to them a wrinkled and bag-like appearance. This, naturally, has been disfavoured by the user and made him prefer, to a certain extent, treated rayon and fabrics made from other fibres in which crease recovery is either naturally superior or has been easily enhanced by treatment. This change-over from cotton is taking place universally, irrespective of the inherent superiority of cotton garments in respect of wear and washability.

A consideration of the mechanism of creasing by Buck and McCord[1] shows that coarse fibres and coarse yarns are inherently more crease resistant than fine fibres and yarns. According to them, coarse cottons, like the Indian cotton and coarse yarns made from them are particularly suitable for crease resisting fabrics. It is therefore necessary to find out how best to utilize this inherent quality of Indian cottons for securing crease resisting fabrics.

Background

Many attempts have been made to improve the crease resistance of cotton and rayon fabrics by chemical finishing treatments with urea-formaldehyde[2] or melamine formaldehyde resins. Investigations have been in progress at the *Shri Ram Institute for Industrial Research*, for quite sometime in arriving

at suitable chemical treatments for improving the crease resistance of fabrics[3]. It is generally observed that a gradual increase in resin pick-up of fabrics increases the crease resistance gradually.

However, great losses in physical properties, such as tear strength, tensile strength and abrasion resistance, accompany any increase in crease resist-ance[4]. An impact tear tester for finding the tear strength of fabrics and useful for assessing the loss in tear strength of resin-treated fabrics, has been developed. The loss in wear life is a constant source of worry for the chemical finisher, and as it appears to be inseparable from the improved crease resistance imparted to the fabric by chemical treatment, one is tempted to strike a compromise and be satisfied with a temporary solution of the problem.

Effect of fabric construction on crease recovery

There is enough evidence[1,4,5] to show that wide variations are possible depending on fabric construction, though no systematic study appears to have been made. Gagliardi and Grentfest[5] experimented with a selected list of fabrics and observed the changes in crease recovery and physical losses using the same chemical treatment. They showed that the degree of improvement in crease resistance is not the same for all fabrics. The changes brought about in other mechanical properties also differ ; some fabrics exhibit excessive reduction in tear strength and in abrasion resistance, while others suffer only moderate losses. It was also found that the original properties of fabrics were restored by hydrolysing the resin employed for increasing the crease resistance within the fibre. For fabrics with inherent crease recovery ranging from 31 to 47 per cent, crease recovery after treat-ment had gone up to 61-76 per cent ; however, increase in crease recovery of any one fabric varied from 33 to 120 per cent depending on the construc-tion of the fabric. Similar variability was also found in the percentage drop in physical properties.

Smith[1] experimented on the crease resistance behaviour of a range of 12 fabrics (arbitrarily chosen), the count range varying from 14s to 100s with some fabrics made of double yarn 2/40s. Even in the untreated state, the percentage crease recovery of the fabrics varied from 47 to 76 per cent while in the treated state, the recovery varied from 82 to 92 per cent. However, the increase in any one fabric due to treatment varied from as low as 13 per cent to as high as 90 per cent. Similarly the drop in tensile strength varied from 18 to 48 per cent while the drop in tear strength varied from 20 to 50 per cent. Similarly, in the course of extensive theoretical studies on the effect of fabric geometry on crease recovery, Hamberger et al.[6] found in a variety of fabrics, a gradual increase in crease recovery depending upon the number of threads removed at the point of crease, the increase amounting to 10 to 21 per cent.

Similar variations have been observed in studies on the effect of fabric construction on crease recovery of other fabrics[7].   However, specific information is meagre and no systematic study has been undertaken in a wide range of counts to arrive at results in regard to (*i*) constructions inherently suitable for crease resistance and (*ii*) constructions particularly suited for chemical treatment—both from the point of view of enhancing crease resistance and from the point of view of reducing loss in physical properties.

Investigations carried out at the Institute have emphasized the need for detailed study to enable the problem to be tackled in a scientific basis.

Conclusion

Though techniques for producing fabrics with outstanding crease resistant properties are available, their application should be related to the intended use of the fabric.   There is no point, for instance, in the maintenance of a certain count in the fabric, when the count necessarily produces a stiff and easily creased cloth and when the elimination of a few ends or picks would contribute to a highly desirable wrinkle pre-product.   On the other hand, when producing a dress fabric, it would be impracticable to try to utilize coarse yarns that go into industrial fabrics, even though the resulting product may resist creasing better.   Therefore, technical, decorative and economic aspects and the inherent advantages of Indian cottons should be kept in view before any particular fabric construction is recommended for imparting crease resistance.

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Role of Moisture in Heat Treatment of Resin-Treated Cellulosic Textiles

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It is common experience in mills that lack of consistent drying of textiles leads to non-uniformity of the finished goods. This is particularly so in the resin finishing of textiles. Though the technology of resin finishing has advanced considerably, and the know-how of the processes involved is well understood, yet the quality of the finished product depends on the experience and judgment of the finisher, in regard to control of conditions, particularly at the drying and baking stage.

The following are the difficulties that finishers encounter in the operations: (i) Non-uniform resin distribution due to non-uniform padding, non-uniform drying, baking and migration of resin ; (ii) excessive losses in the physical and mechanical properties of treated material due to surface deposition of resin, excessive drying and/or baking, improper pH control and choice of catalyst ; (iii) poor wash-fastness of treated materials due to surface resin, incomplete baking and poor catalyst action ; (iv) variation in fabric geometry which affects the degree of drying and baking required and the amount of resin to be applied ; and (v) satisfactory handle and feel, which are entirely personal factors but which nevertheless depend on the factors mentioned above.

The moisture content of the material is an important factor to be taken into consideration during the various stages of operation, particularly drying and baking ; moisture content is responsible for (i) the migration of resin, (ii) obtaining the requisite degree and rate of drying and baking, (iii) catalyst activity and pH control and (iv) physical and chemical modification of fibre material.

FIBRE PROPERTIES AND MOISTURE CONTENT

It is well known that moisture plays an important part in modifying the physical and chemical properties of textile materials, particularly cellulosic

materials, which contain a large number of hydrophillic groups. Increase in the wet tensile strength of cotton and decrease of the same in rayons may be cited as outstanding examples.

Sorption of water by cellulose is due to adsorption and capillary condensation[1]. It is the rigidly held water through strong hydrogen bonding forces which causes hysteresis phenomena[2-4] ; the bonds between cellulose OH groups are broken by water and are not necessarily reformed in the same fashion, thus enabling some water to be entrapped into the structure of the polymer.

It is known that cellulose can contain non-freezable water[5].

These and related phenomena are bound to influence the course of resin polymerization and subsequent physical properties of the treated fibre. For example, it would be interesting to see how far the trapped moisture would help to compensate for losses in tensile strength due to stresses produced by the polymerized resin embedded in the structure ; the trapped moisture may help to plasticize the rigid structure of cellulose after resin treatment so that the crystallites could still be maintained in a mobile condition to impart strength to the fibre[6].

Modification of Fibre Properties during Heat Treatment

Preston *et al.*[7] have shown that thermal treatment of cellulosic fibre leads to distinct modifications depending on the moisture content of fibres. The properties affected are swelling and sorption capacity which decrease to the extent of 50 per cent in cellulose, 30 per cent in silk ; the density increases and this results in increased crystallinity up to 4 per cent in cellulose. At the optimum moisture content, the properties are modified to the maximum during the initial stages of heat treatment.

With increase in temperature the modifications are more pronounced ; after a certain limiting temperature, the tendering of fibre starts. This limit depends on the nature of the fibre but is between 110 and 130°C.

Temperature and moisture content

When a wet textile fabric is subjected to heat treatment, drying proceeds at a constant rate till the moisture content attains a certain critical value, known as the critical moisture content. After this, the rate of drying falls off and there is a rapid rise in the temperature of the fabric depending on the temperature of the source of heat. Therefore, during the period of steady rate of drying, the temperature of the fabric would be the same as the temperature of evaporation of water and thus there would be no risk of excessive temperature being produced on the material before the critical

moisture content is reached[8]. This critical moisture content is a specific property of the fibre, and the moisture (per cent) for various fabrics are the following: Cotton, 25 ; viscose rayon, 28 ; silk, 27 ; and wool, 39.

Beyond the stage of critical moisture content, there is a rapid rise in the temperature of the material, which, unless controlled, damages the fibre.

Migration of solutes and solvents during heat treatment

During the drying of textiles, the solutes applied migrate to the surface at a rate which is determined by the moisture content of the fibre. The greater the initial moisture content, the more marked is the migration, and there is a characteristic limit at which migration ceases. The limits vary from fibre to fibre and from weave to weave[9] and are related to the critical moisture content. The temperature of drying decreases as the moisture mechanically removed increases. Migration is also dependent on the method adopted for heating, such as conduction, convection, radiation or dielectric loss.

Heat treatment of resin-treated textile materials—It is the general practice in heat treatment of resin impregnated textile materials to dry them at low temperatures (80-100°C.) and bake at 120-180°C. The time of baking depends on the temperature and is normally fixed by experience and by the type of equipment available. The following criteria are worth recording: (*i*) Slow drying gives more uniform finish ; (*ii*) rapid drying results in the migration of resin to the surface and imparts a harsh feel and poor end properties to the finished fabric ; (*iii*) slow baking for a long time at low temperature results in improper curing and poor end properties ; (*iv*) short duration of baking at a relatively high temperature results in better curing and the fabric will have soft and fine handle ; (*v*) if the upper limit of temperature is exceeded, there is every possibility of resin hydrolysis as well as loss in physical properties of treated material ; and (*vi*) catalyst efficiency is closely dependent on the moisture content of the fabric and hence on the time and temperature of baking ; therefore, the choice of catalyst must be such as to function within the possible limits of time and temperature[10].

While a slow rate of drying is good to produce even results, it cannot often be practised due to loss in production rate. Naturally one has to arrive at a compromise. This will vary from fibre to fibre and fabric to fabric. In this connection, a general observation made by Bunch[11] is of interest : Bunch points out that the fabric should be dried to an extent greater than the normal regain value (e.g., at 65 per cent R.H. and 70°F.) so that the fabric comes to an equilibrium with the normal moisture regain levels quickly and would be ready for further processing regardless of storage time. On the other hand, if a roll of fabric is bone-dried and left over, it picks up moisture from the selvedge and outer surface, and the high moisture content

of the selvedge and the outer part causes these parts to take a different finish, thus causing non-uniformity of finish.

In baking operations, a long time is sometimes allowed for baking at low temperature due to lack of equipment. In such cases, there is a danger of the fabric being exposed to a temperature higher than that permitted by the critical moisture content. Even then, the temperature may not be sufficient for the catalyst to act and the resin to polymerize. On the other hand, rapid baking at a comparatively high temperature avoids the risk. The limit of high temperature to be attained depends on the moisture content of the fabric before baking.

The action of the catalyst is facilitated by temperature as well as concentration of the catalyst. Both depend on the moisture content of the material[1]. It will be clear from this discussion that the moisture content of the textile material plays a vital role in the resin finishing treatment, and desired effects are produced by controlling the moisture in the material.

SUMMARY

The role of moisture during heat treatment of resin-treated cellulosic textiles has been discussed in order to emphasize the possible avenues of research in this field. A systematic study of the role of moisture in heat treatment of resin-treated cellulosic textiles holds considerable promise in establishing the optimum conditions for producing desired effects.

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Relation between Crystallite Orientation and Mechanical Properties of Mercerized Cotton Fibres. T. RADHAKRISHNAN (Ahmedabad Textile Industry's Research Association, Ahmedabad).

In continuation of the work presented at the 1957 Symposium on Cellulose Research, quantitative results were presented showing the relation between crystallite orientation, tensile strength and extensibility of mercerized cotton fibres belonging to various species. The results show that mercerization tends to minimize the differences between varieties of cotton in regard to tensile properties due probably to the removal of weak links. (*Abstract*)

Structure of Adsorbed Materials on Textile Fibres by Small Angle X-Ray Scattering. T. RADHAKRISHNAN (Ahmedabad Textile Industry's Research Association, Ahmedabad).

Diffraction patterns of many inorganic salts deposited in cotton fibres are shown. It is demonstrated that salts tend to crystallize in the fibre in the form of recognized lattices of the compounds concerned. It is also shown that some salts exhibit preferred orientation when deposited in cotton. A brief account is given of investigations in progress on the determination of the size and shape of crystallites. Small angle X-ray scattering studies have been undertaken in order to determine the size and shape of crystalline aggregates as compared with the size and shapes of individual crystallites. (*Abstract*)

Biosynthesis of Cellulose

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In the course of preparing the review of literature, published during 1956-57, I was struck with the tremendous resurgence of basic and applied work the world over in the field of cellulose research. It is all-embracing, covering the fields of physics, physical chemistry, chemical physics and chemistry, About half of the published literature appears to emanate from U.S.S.R., perhaps mainly an artefact due to the enhanced emphasis by English-speaking countries on covering more efficiently the literature published in U.S.S.R. A great deal of emphasis has been placed on the study of re-actions of cellulose, and the impact of the growing volume of knowledge on high polymer science can be seen in the approach being made in various laboratories. It was a very difficult for me to make a choice as to the aspects that I should cover in this talk. There were two possibilities : (i) To select and highlight a series of advances that had been made in the chemistry of cellulose, including such diverse fields of reactions as cyanoethylation, de-gradation of carbohydrates by alkali, determination of carbonyl groups in cellulose by oximation, and so on or (ii) to pick out a specific wide field and highlight critically the advances in this field. In rejecting the former approach for the latter, my choice was based on the heterogeneity and the Beilstein outlook which would be created by choosing the first method. The talk would essentially be a cataloguing of new reactions and properties of modified celluloses.

Let me quote here from the opening sentences of a paper presented by a Russian chemist. Usmanov, to the 1956 symposium on Macromolecules, held in Israel.

"Of singular importance for modern chemistry is the development of most advantageous processing methods for various raw materials. This is why the chemists of Uzbekistan focus their research on rational utiliza-tion of local raw materials, primarily on cotton, silk, wool and coal. All of them are native polymers and therefore should be investigated by the

methods offered by the study of polymers, which has made considerable progress in the post-war period. We, the Uzbek scholars of polymers, hold as our prime goal further increase in cotton harvest yields and the acceleration of cotton ripening. These problems, as is known, are associated with the biochemical synthesis of cellulose which, sad to say, has not been deciphered thus far ; no one has been able to synthesize cellulose. It is common knowledge that the objective in this case is not synthetic cellulose production, but the discovery of its mechanism of natural synthesis and the opportunities it opens for interference into the development of cotton so as to gain control over its behaviour in the vegetation period."

Sir Robert Robinson, as chairman of a symposium on the *Biogenisis of Natural Products* held in Dublin on September 6, 1957, remarked how the organic chemists' interests in natural products have changed from being an interest purely in structures to one concerned with the origins of such structures. This evolution of a pattern of interests slowly dovetailing various disciplines together again would have been apparent to those of us who started off as structural organic chemists. This was highlighted by the talks delivered by Prof. Richard Kuhn at the 1958 Science Congress session on *Synthesis of Aminosugars*.

Greathouse in 1957 came out with a publication on the *Isolation of a cell-free enzyme system from Acetobacter xylinum capable of cellulose synthesis* and my talk today takes its cue from this break-through, from the chemist viewing a physiological process culminating in the synthesis of a poly-saccharide to synthesizing a polysaccharide (cellulose) in a test tube by pure cell-free enzyme systems. Of course, answers to all the questions implicit in Usmanov's statement, referred to earlier, have not been forthcoming but the break-through has been made.

Two main streams of work have progressed in this field of biosynthesis of cellulose : (i) Synthesis of cellulose by the cotton plant and (ii) synthesis of cellulose by microorganisms. In turn, both these streams have had certain main objectives, i.e. How does the synthesis of cellulose take place? What are the precursors, and what are the mechanisms by which carbon in the form of monosaccharides is polymerized or made to combine? Generally, the pattern of work has been similar to most biosynthetic work in recent years, i.e. utilization of labelled C^{14} precursors, and meticulous follow through on the stages of build-up. Recent advancements on radiochemistry of carbon atoms have been a great help in unravelling this story.

SYNTHESIS IN COTTON PLANT

Russian work

Usmanov[2] used pure cellulose from fibres, obtained by the method of Corey and Gray[3].

Small quantity early age cellulose determinations which were conducted by $C^{14}O_2$ introduction into young bushes resulted in the formation of spotted cellulose in the fibre which facilitated its detection and quantitative determination after separation from accompanying substances. The degree of polymerization (D.P.) of differently aged cellulose samples extracted from the plant was determined by means of the Ubbecohde viscometer with the use of purest nitrogen, entirely free from oxygen.

The structure of cellulose during the vegetation period was studied by sorption tests, heat of wetting by water and other liquids, and the values of strength and elongation in bone dry and wet conditions in a specific vacuum dynamometer.

Cellulose accumulation in cotton boll and fibre

There are two schools of opinion: (i) Those that hold that in the first period (16-75 days) the fibre mainly consists of only the cuticle[1] and (ii) those who say that if cotton fibre is thoroughly separated from impurities, X-ray pattern of a 6-day old fibre shows the presence of cellulose[5].

Fig. 1-4 show the rate of formation of cellulose in a cotton boll after fertilization of the flower. Cellulose is present within a few hours after fertilization and steadily reaches the peak rate of formation by about the
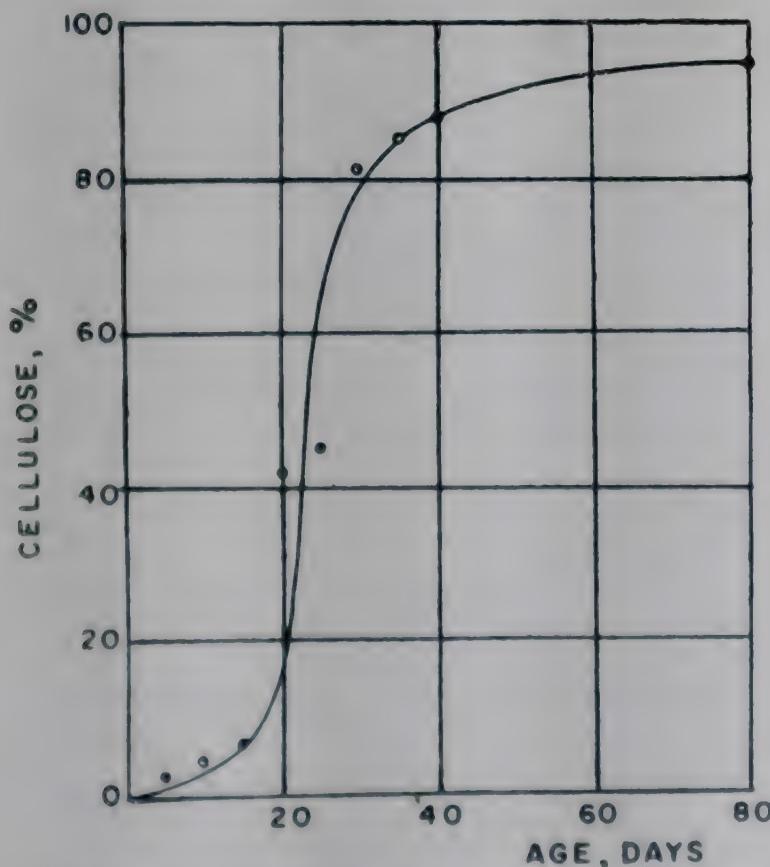
FIG. 1—RATE OF FORMATION OF CELLULOSE IN BOLL TYPE 1306 DV

twenty-fifth day.   Also, by about the same time most of the cellulose present
is transformed to X-cellulose, i.e. it acquires a high degree of polymeriza-
tion and is in sufficiently dense molecular packing.   Also during this time
the concentration of glucose and fructose begins to fall and by the twenty-fifth
day reaches a minimum[6].

The change of cellulose structure with ageing was detected by determination
of its sorption ability in a spring sorption balance and the heat of wetting
in an adiabatic calorimeter[7].   The values of cellulose sorption and heat of
wetting diminish with age until 40 days from the day of flowering and after
the fortieth day begin to increase.   This shows that the density of structure
packing in native cellulose initially grows and then diminishes.

Using sorption and calorimetic data, the Russian workers determined certain
thermodynamic values from the equivalent of water vapour present over
cellulose in a sorption balance.   The free energy for different moisture
contents in cellulose was calculated, while the water entropy during its
sorption with cellulose was calculated with the use of differential sorption heat
values determined calorimetrically.

FIG. 2—RATE OF FORMATION OF CELLULOSE AND ALPHA-CELLULOSE IN COTTON FIBRES
TYPE 108-F
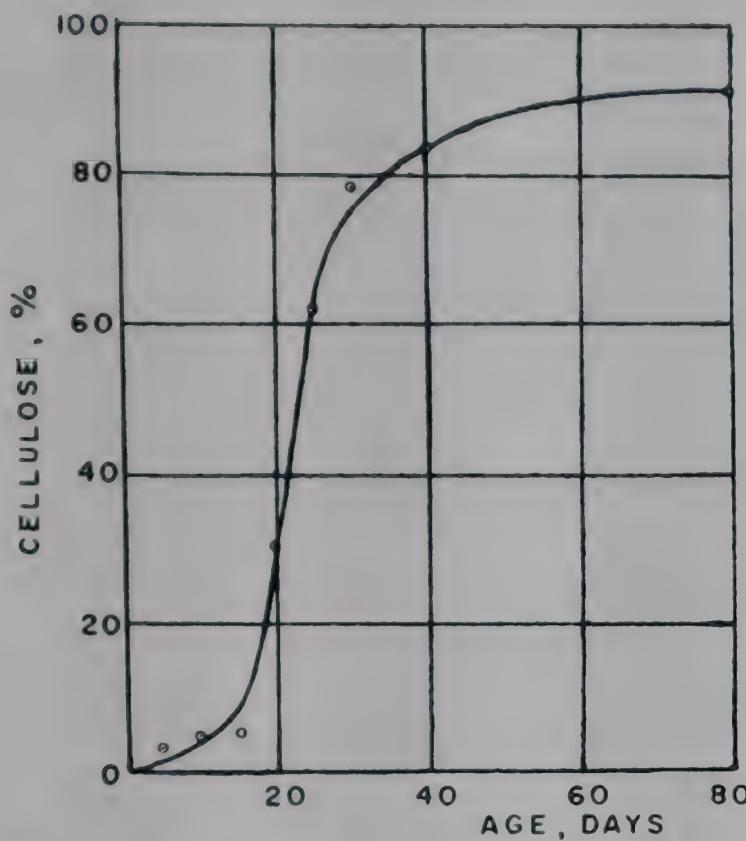
FIG. 3—RATE OF FORMATION OF CELLULOSE IN COTTON FIBRES TYPE 4028

Fig. 5 shows that entropy first increases, then decreases. This feature is characteristic of cases of limited swelling. This increase in cellulo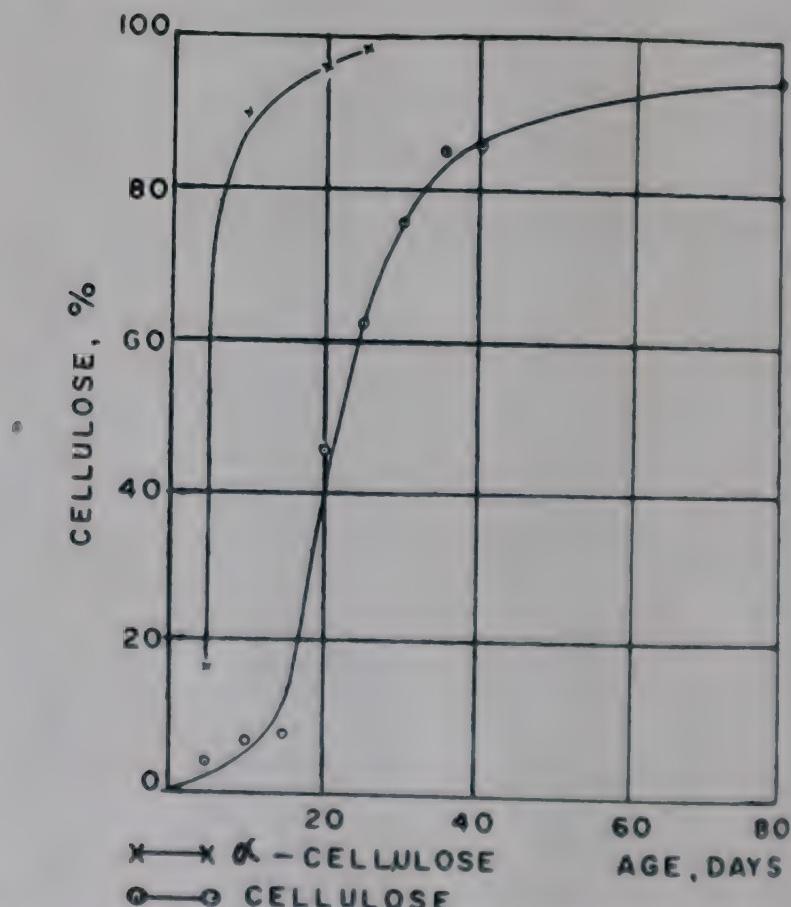se density with ageing is also demonstrated by the increasing difficulty in hydrolysing with sulphuric acid as the age of the fibre increases.

Fig. 6 shows the changes in the degree of polymerization of cellulose with time after flowering. The polymerization of cellulose increases rapidly at the initial stages of the fibre growth, then slows down and reaches a constant value by the time of the ripening of the boll. The faster the ripening, the sooner is the consistency of D.P. established. The authors claim that D.P. is the genuine index for cotton fibre ripening. The fact that initially low molecular cellulose is present which changes to high molecular cellulose with fibre development seems to confirm the polycondensational mechanism of the origin of cellulose in nature. Based on all these data this school of workers propound the theory that the synthesis of cellulose takes place throughout the fibre, both in the inner fibre space filled by the protoplasm and within its secondary wall, which is already taken up by loose cellulose. This may explain the gradual increase in the density of cellulose until it reaches a maximum and the increase of molecular weight to a constant value, then the decrease in its density of packing at the expense of the splitting action of the ends of the chains of cellulose which grow during the synthesis, which should have brought to a breakdown a part of the intramolecular bonds.

6
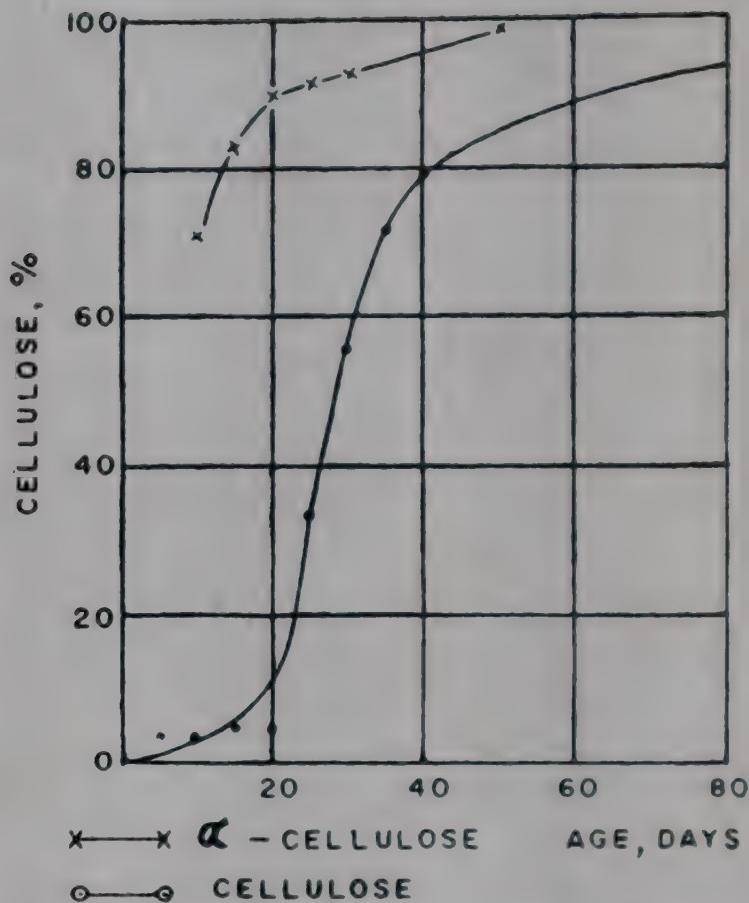
FIG. 4—RATE OF FORMATION OF CELLULOSE AND ALPHA-CELLULOSE IN COTTON FIBRES
TYPE 2-1-3

American work

While paying a tribute to this well-planned and well-directed team work culminating in the Uzbek workers' findings on the formation of cellulose in the boll after inflorescence, we must not forget the basic problem of the method by which this cellulose is synthesized. I have already referred to earlier work of Anderson and Kerr[5] that the primary cell wall of the cotton fibre is formed and reaches its full length during the first 20 days or so following the fertilization of the flower. The Russian work has also demonstrated that although the formation of cellulose within the fibre is not fast during this period, traces of cellulose are present immediately after fertilization of the ovary. In U.S.A., Greathouse of the University of Florida together with Isbell of the *National Bureau of Standards* and Milton Harris and his colleagues of *Harris Research Laboratories* started on an ambitious programme of work on the biosynthesis of cellulose by *Acetobacter xylinum*. They carried out work on a cotton plant using their experience of utilizing 1-C^{14} labelled glucose in this work and assuming on very reasonable grounds that at the time of optimum sugar translocation through the plant vascular system, labelled glucose should be capable of forming the brick in a cellulose chain. It had already been well established that the reducing sugar content of the cotton boll is 60-70 per cent between the time of pollination of the

flower and 21 days following the fertilization. The best utilization of C^{14} glucose should be at the time of the greatest conversion of reducing sugars to cellulose. It is seen from the earlier graphs that Russian work had shown that this takes place between 20 and 25 days after pollination.

The experimental procedure followed by Greathouse and his collaborators is as follows: Plants (Stoneville 2B) grown in 6 in. pots in a green house of the United States Department of Agriculture were allowed normal growth until they flowered. The stem just below the boll was sliced longitudinally with a razor blade and the cut portion immersed in sugar solution. The selected plant was not watered before treatment until the plant showed loss of some turgor and then watered approximately 30 min. before introducing glucose-1-C^{14}. The sugar solution was taken into the boll within a few min., the rate of transfer varying with the sugar content of the boll at the time of experiment. Stem and boll were subsequently carefully taped to prevent any further damage or injury. The first series of experiments carried out by introducing the glucose on the same day as pollination, and harvesting on the twenty-first day showed that after dewaxing and extracting with 1 per cent sodium hydroxide solution the small quantity of cellulose showed negligible radioactivity. When the rest of the boll was extracted it showed presence of most of the radioactivity introduced as glucose-1-C^{14}.

In the second series of experiments, 12.5 Hc of glucose-1-C^{14} was introduced by a similar method under a 21-day old boll. The boll was allowed to mature
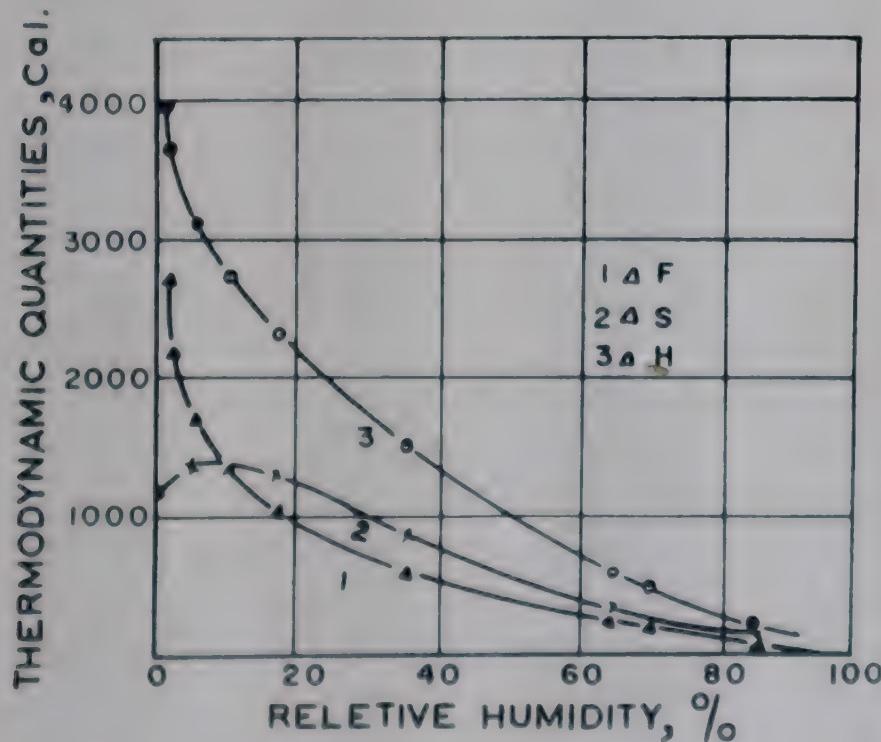
FIG. 5—THERMODYNAMIC QUANTITIES OF CELLULOSE AS A FUNCTION OF RELATIVE HUMIDITY

for a further 30 days, fibres harvested from the seeds and dewaxed with ethyl alcohol in a soxhlet for 5 hr for quantitative removal[8]. They were then dried and alkali boiled (1% NaOH for 1 hr) precautions being taken to prevent oxidation ; washed with 300 ml. dilute acetic acid, then with water until free of acid and dried at 50°C. for 2 hr in a circulating air oven. The yield which was 406 mg. of purified cellulose was hydrolysed by the method of Monier-Williams[9], when 337 mg. of unpurified sugar was recovered. This was dissolved in 5 ml. of water and 0.01 ml. was estimated for C^{14} content by the direct method developed by Schwebel et al. This showed that 5.49 Hc of C^{14} were present in the 5 ml. of sugar solution, showing conversion of 44 per cent radioactive C^{14} into cellulose. It was also proved by sorption on Darco G-60 & Celita and elution with water that 95 per cent of the cellulose had been hydrolysed to glucose by the Monier-Williams method. It was also demonstrated that 99.97 per cent of the radioactivity present as C^{14} was in carbon 1 of the glucose molecule, by oxidising the glucose with oxygen in aqueous potassium hydroxide and oxidising the resulting potassium D-arabonate to carbon dioxide, and determining its activity by the use of a vibrating reed electrometer.

This work provided the first experimental evidence of the course of synthesis from glucose to cellulose indicating that glucose is polymerized directly, perhaps receiving its essential energy through phosphorylation.

FIG. 6—DEGREE OF POLYMERIZATION (D.P.) OF CELLULOSE AS A FUNCTION OF TIME OF GROWTH

Microorganisms

Having covered the work carried out so far in the field of plant synthesis of cotton, let us now look at the work carried out on unicellular organisms, *Acetobacter xylenum* by the American group of workers, and *Acetobacter acetigenum* by the British school. For this review I am using mainly the results of Greathouse and his associate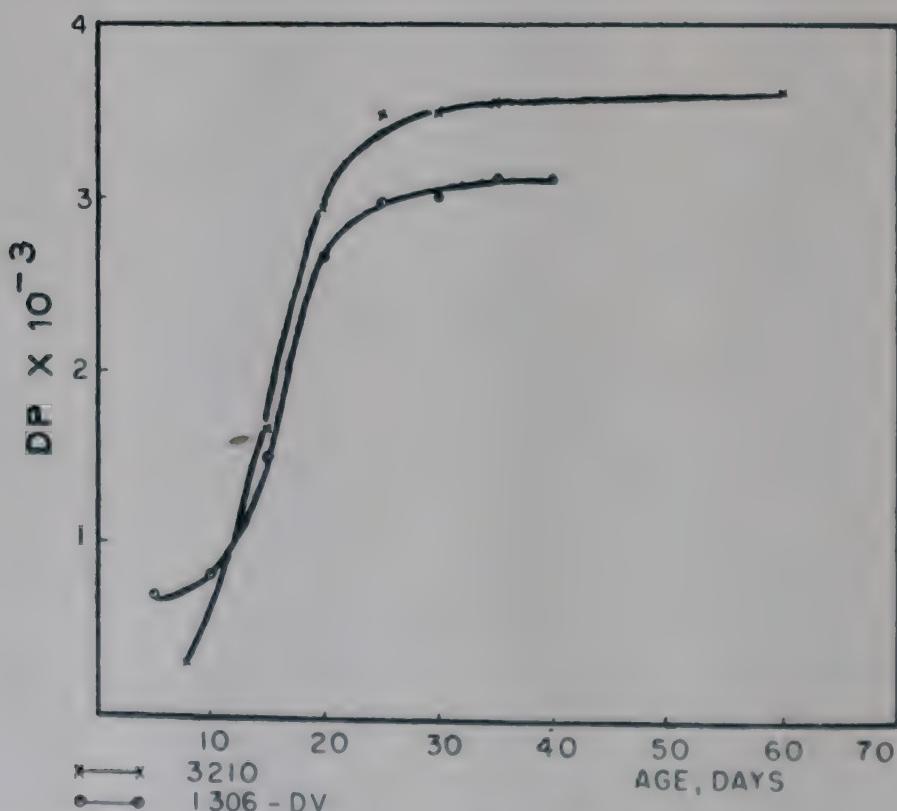s who have demonstrated the synthesis of cellulose from D-glucose-1-C^{11} by a cell-free enzyme/enzymes system isolated from *A. xylenum*.

Whether or not cellulose is synthesized from glucose by identical methods in both plants and unicellular organisms, the choice of unicellular organism for preliminary studies appears obvious from the point of view of (*i*) controlled conditions of experimentation, (*ii*) rapidity with which they grow and produce metabolites, (*iii*) generally far simpler mechanisms involved, etc. As early as 1886 Brown[10] reported the biosynthesis of cellulose by *A. xylenum*. Hibbert and Baisha published during 1931-38 a series of papers demonstrating the chemical identity of the bacterial product with cotton cellulose. The product on hydrolysis with 2N hydrochloric acid gave glucose quantitatively. The triacetate with methyl alcohol + hydrochloric acid gave methylglucoside in 94.3 per cent yield. The triacetate after purification was found to be identical with the triacetate prepared from cotton cellulose. Methylation of the triacetate followed by hydrolysis of the trimethyl ether yielded methyl 2,3,6-trimethylglucoside and this on hydrolysis yielded crystalline 2,3,6-trimethylglucose. A chloroform solution of the triacetate yielded on dry spinning a cellulose acetate fibre, identical with cotton cellulose acetate fibre. On hydrolysis (alc. sodium hydroxide) of the acetate fibres the regenerated cellulose gave an X-ray diagram with the typical diffraction pattern of natural cotton cellulose. Also, work by Mark, Eggert and others comparing X-ray patterns of bacterial cellulose with cotton cellulose has shown identity with each other. In 1949 and later, this confirmation was sustained by the work of Mühlethaler[11] using electron diffraction methods and by Shirk and Greathouse using infrared spectral techniques. On these grounds the choice of *A. xylenum* for studying the processes of biosynthesis of cellulose appears sound. Mühlethaler had also presented evidence based on electron microscopic studies of *A. xylenum* that the formation of cellulose by this bacterium probably does not take place within the cell or from its surface, but rather at some distance from the organism.

The work in this field by the American school can be broadly divided under 3 major headings: (*i*) Role of ethanol on the biosynthesis of C^{11}-cellulose from D-glucose-1-C^{11}, (*ii*) investigations into the utilization of glycerol, acetates, and glucose labelled with C^{11} and unlabelled in the synthesis of cellulose; and (*iii*) isolation of cell-free enzymes from *A. xylenum* and its role in the synthesis of cellulose. In all this work cumulative evidence was also gathered on the steps of biosynthesis.

Schramm, Gromet and Hestrin of the Hebrew University have carried out investigations on the biosynthesis of cellulose by *A. xylenum*.   Both schools of workers have used the same basic principles, i.e. use of specifically labelled C^{14}-glucose provided by Isbell and the methods developed by him and his colleagues for estimating the C^{14} activity[12].   This requires the conversion of carbon dioxide to barium carbonate and the determination of its radioactivity, and the determination of total C^{14} content in cellulose by wet ashing and absorbing all carbon dioxide to form barium carbonate.   Finally the C^{14} in residues including the material obtained from the purification of cellulose is determined by counts on dried aliquots after adjustment to pH 7-8.

When the position of the label in the cellulose structure was to be determined, the C^{14} content of the cellulose was calculated from the count of the hydrolysate prepared by the method of Monier-Williams.

Location of C^{14} in cellulose—The following method was adopted for the location of C^{14} in cellulose:

Glucose   5-Hydroxymethyl-2-furfuraldelyde
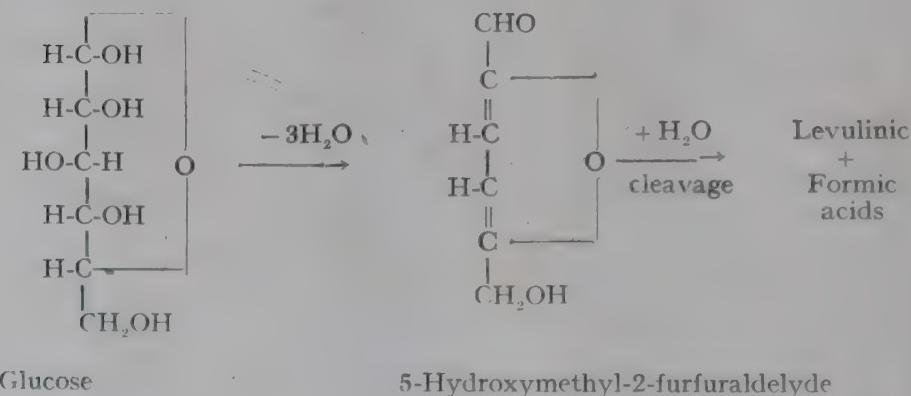
After hydrolysis to glucose, 1-C^{14}-D-glucose was hydrolysed with hydrobromic acid to give traces of humins + levulinic acid and a quantitative yield of formic acid containing all the radioactive C^{14} at position 1 of the glucose[13].   2-3 C atoms were obtained by using the potassium D-levulinate from 1-C, analysis and preparing its benzimidazole[14].   The activity at position 3, positions 4 & 5 together and positions 1 through 5 inclusive was determined by oxidation with lead tetracetate[15].   Carbon atom 6 was obtained by oxidation with periodic acid, of the C_6-carbon to formaldehyde and its conversion to the dimedone derivative.   Counts were made by plating.

Table 1 shows the yield of cellulose obtained together with metabolic products with and without ethanol.   It will be seen that there is really a six-fold increase in the utilization of C^{14} in the synthesis of cellulose and a three-fold

increase in the quantity of cellulose produced. Most of the ethanol appears to be used up in the production of carbon dioxide.

Table 2 shows the specific radioactivity values of culture products. Table 3 shows the location of the label in the structure of glucose units. Although the major portion of the label was found at position 1, appreciable quantities are found at positions 3 and 4. This indicates that in the synthesis of cellulose, three carbon intermediate scission products may be involved. The

TABLE 1—YIELDS OF CULTURE PRODUCTS

	D-Glucose-1-C^{14}		D-Glucose-1-C^{14} + ethanol	
	Yield mg.C	C^{14}yield %	Yield mg.C	C^{14}yield %
D-Glucose	80.1	. .	80.8	. .
Cellulose	2.1	0.55	6.6	3.7
Carbon dioxide	56.8	76.0	119.0*	58.4
Liquid products	21.0	23.4	34.5	38.6

* Medium contains 79.3 mg. of ethanol carbon, and this accounts for the high yield of CO_2.

TABLE 2—SPECIFIC RADIOACTIVITY VALUES OF CULTURE PRODUCTS

	D-Glucose-1-C^{14} microcuries/ mg.C.	D-Glucose-1-C^{14} + ethanol, microcuries/ mg.C.
D-Glucose-1-C^{14} supplied	0.34	0.36
D-Cellulose-C^{14} obtained	0.071	0.16
Carbon dioxide	0.37	0.14*

* Considerable part of CO_2 comes from ethanol in medium ; this accounts for low specific radioactivity

TABLE 3—LOCATION OF LABEL IN STRUCTURE OF GLUCOSE UNITS IN BACTERIAL CELLULOSE

STRUCTURE POSITION	D-Glucose		D-Glucose + ethanol	
	Millimicrocuries per mM.*	%	Millimicrocuries per mM.*	%
1	53.0	82.2	65.7	70.0
2	0.4†	0	−0.5†	0
3	7.0	10.8	14.1	15.0
4	5.6	8.7	12.9	13.7
5	−0.1†	0	1.3	1.4†
6	0.6†	0	1.5	1.6†

* Found by analysis after dilution with carrier glucose   † Within the limits of experimental error

fact that there is no activity in position 6 would appear to indicate that the triose fragments formed by the usual glycolytic process are not involved since such a mechanism would result in activity in the 6 position. The pattern of the label distribution, i.e. 1,3,4 positions for both ethanolic and non-ethanolic culture media appears similar.

It also appears that where glucose is not the only source of carbon, and easily oxidizable substrates like ethanol are present more of the label enters the cellulose molecule. When compared with data presented earlier on the formation of cellulose in the cotton boll there appears to be two different pathways from intact labelled D-glucose.

Table 4 shows the utilization of labelled acetate or ethanol in an unlabelled D-glucose enriched medium when one of each of ethanol-1-C^{14}, ethanol-2-C^{14}, sodium acetate-1-C^{14} and sodium acetate-2-C^{14} were used as the sole labelled ingredient. Experiments 1-4 based on similar techniques of C^{14} assay, show (as in earlier Tables) traces of activity although they are not significant.

TABLE 4—UTILIZATION OF LABELLED ETHANOL AND SODIUM ACETATE

EXPERI-MENT No.	LABELLED SUBSTRATE	TOTAL C^{14} IN CULTURE, Micro-curies	C^{14} FOUND IN CO_2, Micro-curies	C^{14} FOUND IN CELLULOSE, Microcuries
1	Ethanol-1-C^{14}	14	14	0.005
2	Ethanol-2-C^{14}	14	13.5	0.04
3	Sodium acetate-1-C^{14}	19	14.6	0.12
4	Sodium acetate-2-C^{14}	16	10.8	0.18
5	Ethanol-1-C^{14}	33	21	None
6	Sodium acetate-1-C^{14}	46	36	0.0003
7	Sodium acetate-2-C^{14}	79	68	0.006

TABLE 5—LOCATION OF LABEL IN D-GLUCOSE FROM BACTERIAL CELLULOSE

STRUCTURE POSITION	D-GLUCOSE-1-C^{14} ADDED 0 HR	ADDED 24 HR LATER
1	62.5	79.1
2	1.6	0.4
3	19.2	11.0
4	15.4	8.0
5	0.9	0.4
6	0.4	1.1

TABLE 6—SUBSTRATE, YIELD OF PRODUCTS AND C¹⁴-LABEL DISTRIBUTION

Substrate	Wt, mg.C	Label C¹⁴ %
D-Glucose-6-C¹⁴	80.5	100
Ethanol	79.3	None
Product		
Carbon dioxide	111.0	28.9
Cellulose	32.6	23.8

TABLE 7—LOCATION OF LABEL IN GLUCOSE FROM BACTERIAL
CELLULOSE SUBSTRATE, D-GLUCOSE-6-C¹⁴

Structure position	%
1	9.3
2	1.7
3	3.9
4	. .
5	3.5
6	81.6

TABLE 8—SUBSTRATE, YIELD OF PRODUCTS AND C¹⁴-LABEL DISTRIBUTION

Substrate	Wt, mg.C	Label C¹⁴ %
Glycerol-1,3-C¹⁴	98.0	100
Ethanol	79.3	None
Product		
Carbon dioxide	87.4	6.1
Cellulose	11.8	5.7

TABLE 9—LOCATION OF LABEL IN GLUCOSE FROM BACTERIAL CELLULOSE
SUBSTRATE, GLYCEROL-1,3-C¹⁴

Structure position	%
1	12.7
2	3.7
3	21.7
4	28.9
5	3.0
6	30.0

However, experiments 5, 6 and 7 were carried out using more elaborate puri-
fication procedures and a more sensitive measuring instrument. These results
show that the trace activities must have been due to non-cellulosic impurities
and that while ethanol and acetate are extensively metabolized neither of
these 2-carbon compounds nor any fragments thereof appear in the cellulose
formed. In the presence of D-glucose the enhanced yield of cellulose must
be due to some other cause.

The results when D-glucose-1-C^{14} was added to the culture medium at 0 hr
and 24 hr after incubation are shown in Table 5. The label in D-glucose
C^{14} was distributed over the six positions in the glucose units. The delayed
addition produces a 10-12 per cent higher concentration of the label in
the original position 1.

Tables 6 and 7 show the results obtained when D-glucose-6-C^{14} was used in
the substrate and the location of label in glucose from bacterial cellulose.
The major portion (81.6%) was located at position 6, corresponding to its
position in the labelled substrate.

Data on the utilization of glycerol-1,3-C^{14} as the sole carbon source are
presented in Table 8. To highlight the significance of these data it will be
seen that (i) very small activity is present in carbon dioxide showing that
most of the carbon dioxide is derived from ethanol and very little from glyce-
rol, (ii) that the amount of cellulose formed from a triose like glycerol is
considerably less in the 7-day incubation period, (iii) that (Table 9) the
label in the cellulose is distributed over all the 6 positions in glucose units
with smaller quantities being in positions 2 and 5. It has subsequently been
shown that when cellulose has to be synthesized exclusively from trioses by
these bacteria, the time required for the enzyme system to produce sizeable
quantities of cellulose intermediates (hexoses, hexose phosphates, etc.) exceeds
the 7-day incubation periods used in these experiments.

In all the cases of cellulose biosynthesis presented so far some of the original
hexose units are apparently cleaved prior to cellulose formation. The con-
centration of the label in the original position depends primarily on the origi-
nal position of the label and the time of adding the radioactive sugar. At
least two major mechanisms as shown in Fig. 7 appear possible: (i) Direct
polymerization possibly involving phosphorylation and (ii) cleavage of the
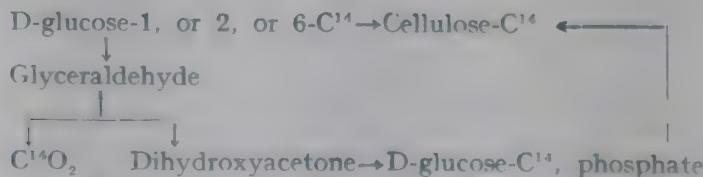
D-glucose-1, or 2, or 6-C^{14} →Cellulose-C^{14} ←————
         ↓
Glyceraldehyde
        ↓
————————
↓   ↓
$C^{14}O_2$ Dihydroxyacetone→D-glucose-C^{14}, phosphate

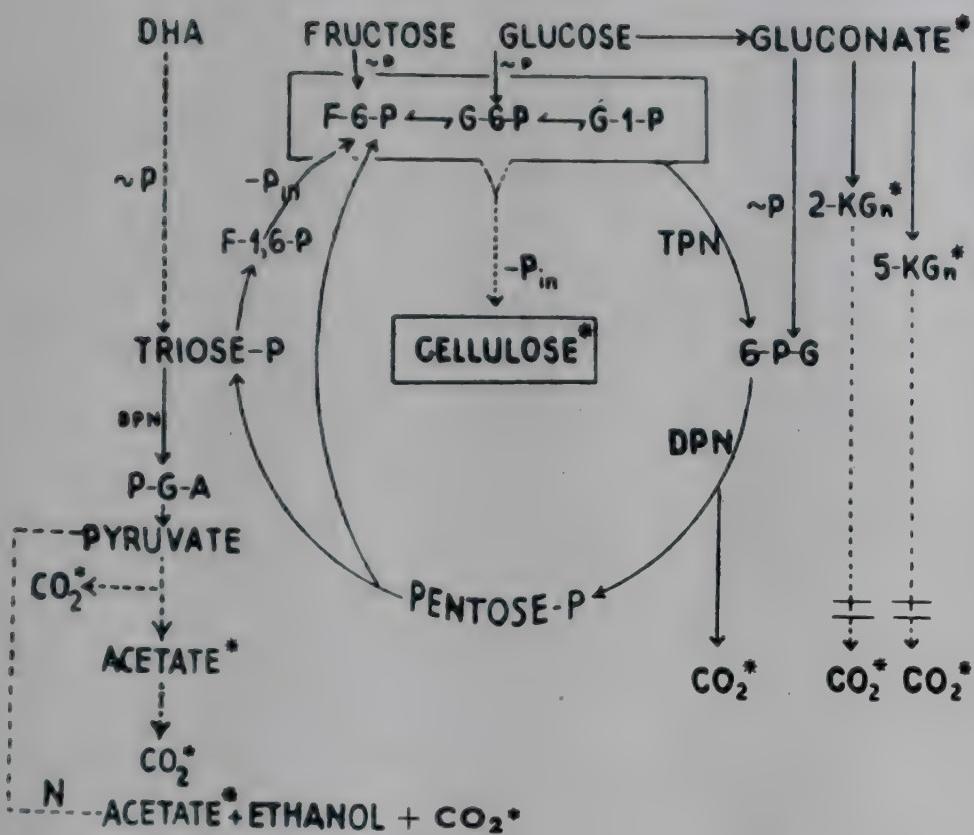FIG. 7—MECHANISM OF CELLULOSE BIOSYNTHESIS

FIG. 8—PRODUCTION OF CARBON DIOXIDE AND CELLULOSE BY *Acetobacter xylinum*
[—→ reactions that have been carried out in cell-free extract of the bacteria ;
.....→ reactions which have not as yet been carried out in the cell-free system ;
— ‖ —→ relatively slow reactions ; * the formation of the products in the medium
of cell suspensions have been demonstrated by a direct analytical method ;
N—anaerobic pyruvate dismutation] Fructose was inert towards the glucose-grown
cells but was metabolized by fructose-grown cells to the products shown. Phosphate
esters (glucose-6-phosphate, α- and β-glucose-1-phosphate and uridine diphospho-
glucose were not metabolized by the whole cells. As extracts oxidized glucose-6-
phosphate and α-glucose-1-phosphate readily, it is assumed that these phosphate
esters are inert when added to a cell suspension only because they fail to enter the cell

hexose and resynthesis of the hexose phosphates from trioses such as glycerol.
Hexose phosphates have been isolated and identified by Greathouse *et al.*
as intermediates in the biosynthesis of cellulose from D-glucose.

The American group of workers have used in their investigations a substrate
containing yeast extract (0.5-2 per cent) and ethanol. During 1957,
Schramm, Gromet and Hestrin[5] studied this synthesis using washed non-
proliferating cells of *A. xylinum* on the basis that the American work had
been carried out under conditions where the cells were growing in a culture
medium containing several carbon sources. Otherwise the approach was
similar, but the test system consisted of non-proliferating washed cells in a
solution containing only one added carbon source (glucose or fructose).
Based on a school of thought of Cheldelin, King *et al.*, that dissimilation of
carbohydrate in *Acetobacter* species is largely via the pentose cycle, three
lines of investigation were undertaken : (*i*) determination of the relative rates
and balance sheets of oxidations of carbohydrates and their conversion to

TABLE 10—OPTIMUM pH OF ENZYME SYSTEMS CAPABLE OF CELLULOSE SYNTHESIS

pH	CELLULOSE YIELD mg.	pH	CELLULOSE YIELD mg.
5.0	0.40	8.0	34.30
5.5	0.82	8.5	48.04
6.0	4.71	9.0	47.35
6.5	12.34	9.5	32.50
7.0	19.85	10.0	0.25

TABLE 11—EFFECT OF ADDING ATP TO THE MEDIUM ON CELLULOSE YIELD

[temp., 30°C ; pH, 8.5]

ATP g.	CELLULOSE YIELD mg.	ATP g.	CELLULOSE YIELD mg.
0	0.2	0.10	43.4
0.02	10.5	0.20	45.1
0.04	18.7	0.40	44.8

cellulose by cells (*ii*) radioactive tracer analysis of these processes and (*iii*) analysis of intermediary steps by sugar dissimilation effected in a cell-free system. Fig. 8 shows their principle findings.

A. xylinum oxidizes glucose rapidly to gluconate and the latter is then slowly oxidized to *beta* gluconates. In addition, the cells possess a fluoride resistant phosphorylative system whereby glucose and gluconate can be oxidized readily to carbon dioxide. Carbon dioxide arises in *A. xylinum* largely via a pentose cycle formed by oxidative decarboxylation of 6-phosphogluconate and from which triose phosphate is withdrawn by oxidation via phosphoglyceric acid to pyruvate. The latter is oxidized to acetate and then via a fluoracetate sensitive pathway to carbon dioxide. Hexose phosphate arises both directly by phosphorylation of exogenous hexose and from pentose cycle intermediates, and gives rise to cellulose.

Greathouse has isolated a cell-free enzyme system from *A. xylinum* capable of cellulose synthesis. In this series of experiments the enzyme was isolated from a 48-hr old culture by standard methods modified by disrupting the cells with abrasives as well as mechanical means. In all stages both culture and microscopic methods were used to check the absence of cells. The isolated, lyophelized, freeze-dried crude enzyme was made up to a 10 per cent solution and 2.5 ml. of this solution added to 25 ml. of sterilized liquid

medium containing glucose (1%), yeast extract (2%), potassium dihydrogen-phosphate (0.10%), ethanol (0.5%) + 0.1 per cent adenosine triphosphate (ATP). Enzymatically synthesized cellulose was formed in 2-4 hr at $30°$ incubation. No contamination was found. Ether was used on the surface of the culture medium to prevent contamination.

It is seen from Table 10 that the optimum pH is 8.5. No cellulose is formed without the addition of ATP and optimum results were obtained with the addition of 0.2 g. of ATP (Table 11). The energy for this possible direct polymerization of glucose or glucose phosphate to cellulose by the cell-free enzyme system is likely to be provided by phosphorylation through high energy phosphate bonds of ATP. The yield of cellulose based on the D-glucose-1-C^{14} was approximately 15 per cent. D-glucose-1-C^{14} obtained by hydrolysis of this cellulose was oxidized by oxygen in aqueous potassium hydroxide to remove carbon 1 when 96.7 per cent of the activity present was removed in the carbon dioxide by determining the activity of purified potassium D-arabonate left after removing carbon 1.

The results of the work carried out by the American workers fit in very well with the proposed cycle of Schramm and his colleagues. While the details of Schramm's work are not available, it is difficult to interpret the disparities between the work of the two schools, but by and large the small yields in the enzyme synthesis demonstrated by Greathouse *et al*. do not preclude the cycle proposed by Schramm. In fact they fit in well into this cycle. Greater clarity will ensue when further details of the enzyme synthesis in terms of carbon balance are published.

In this rather long survey of literature in a limited field I have attempted to underline mainly the fascination that research in biosynthesis can produce. It is quite likely that when more is learnt of the mechanism of biosynthesis of cellulose, more methods will be available to the applied worker to enhance yields of cellulose in nature, to shorten the maturing time of crops and even perhaps to partially synthesize cellulose.

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Modification of Jute Fibre Properties by Esterification and Etherification

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Every natural or artificial fibre has specific and limited practical uses which depend upon its physical and chemical characteristics. There is a tendency, however, in recent years with the advancement of fibre science and techno- logy, to modify the properties of a textile fibre by chemical treatments for extending its use. These treatments are generally based on modification of the reactive OH groups (with the production of chemical derivatives). Cellu- lose, which is the main structural basis of a vegetable fibre, is known to contain both primary and secondary OH groups. The OH groups which are present in the more accessible portion of the fibre, i.e. the non-crystalline region, are in most cases, more reactive than those occurring in the crystal- line region. The reaction mechanism, however, appears to be more com- plicated in the case of a lignocellulosic fibre, such as jute, than in the case of a relatively pure cellulosic fibre, like cotton, because of the complexity of its chemical composition and the presence of other types of hydroxyl groups.

Basically, jute fibre is composed of approximately 60 per cent cellulose, 24 per cent hemicellulose, 13 per cent lignin and 3 per cent other minor consti- tuents. The hemicellulosic components are known to contain mainly secon- dary alcoholic OH groups, while lignin is believed to be associated both with alcoholic and phenolic OH groups. Besides, as the chemical nature and the physical structure of jute are considerably different from those of relatively pure cellulosic fibres, the nature of the problem with jute and the scope of modifying the properties of this fibre are to some extent different from those of cotton or allied fibres.

As a textile fibre, jute has a number of disadvantages of which the most serious one is that its colour, both in the untreated and bleached state, is not permanent, but changes to yellow and then to brown, slowly in diffused light and rapidly in direct sunlight, the effect being commonly known as yellowing. This colour change is much less important when jute is employed

as a packing material, but restricts its use as a furnishing or a utility material liable to prolonged exposure to light.

It has been shown by Callow and Speakman[1] that yellowing or photochemical discolouration of jute is mainly due to the transformation of the lignin component into coloured derivatives, possibly of quinonoid type. Partial acetylation which results in blocking reactive OH groups of jute, including those occurring in lignin, has been shown to inhibit the yellowing ; and if the acetyl content is sufficiently high, the material is actually bleached during exposure to light. Further, it has been observed[2] that the minimum acetyl content which is necessary for the prevention of yellowing varies from 14 to 19 per cent, depending on the condition of acetylation as well as on the nature of the catalyst employed. The bleaching action of the highly acetylated material has, however, been attributed to the formation of acetyl peroxide.

It has been found that the acetyl group in acetylated jute is not very stable, but hydrolyses slowly on exposure to light. It is expected, however, that a more permanent product will be obtained on etherification of the reactive OH groups. Both partially esterified and etherified fibres, in addition to their resistance to light, are likely to be more resistant to heat and rotting, besides having lower affinity for moisture and considerable alteration in dyeing properties.

(i) *Acetylation of jute*—The methods which have so far been employed for the acetylation of jute are based on heating the material at a high temperature (about 100°C.) with acetic anhydride, alone or in mixture with an inert solvent, in the presence of a catalyst. During acetylation, bleached jute has been found to undergo a high degree of discolouration possibly due to high reaction temperatures. The effect of various catalysts on the acetylation of jute at a lower temperature is being studied with a view to obtaining a product with minimum discolouration.

Since it is difficult to recover quantitatively the unreacted acetic anhydride from spent liquor (because jute dissolves in the acetylating medium), it appears that the process will be more straightforward and simple if the acetylation is carried out in the vapour phase. A systematic study is therefore being carried out on the vapour phase acetylation of jute with a view to finding out a suitable catalyst and optimum conditions for the reaction. The properties of the acetylated fibre with varying acetyl contents prepared in the vapour phase will be compared with those obtained in the liquid phase.

The extent of acetylation in jute is measured by hydrolysing the material with caustic soda and estimating the liberated acetic acid.

(*ii*) *Cyanoethylation of jute*—Of the different methods available, it is proposed to employ the cyanoethylation method for the etherification of jute. Significant improvements in the properties of cotton subjected to this reaction have recently been reported. Although ether groups, in general, are extremely resistant to atmospheric influences and chemical treatments, the cyanoethyl group which is more resistant than the acetyl, is not highly stable due to the presence of the nitrile group. The nitrile group on treatment with strong alkali is converted into carboxyl along with considerable splitting of both cyanoethyl and carboxyethyl groups.

No work seems to have been carried out on the cyanoethylation of jute or any other lignocellulosic fibre and it is rather difficult to visualize, at this stage, the reactivity towards cyanoethylation of OH groups of jute constituents, particularly lignin. It is therefore considered worthwhile to make a systematic study on cyanoethylation of jute and examine the properties of the modified fibre.

The usual method of cyanoethylation consists in treating the material with acrylonitrile in the presence of an alkaline catalyst[3]. Since the hemicellulosic constituent is highly sensitive to alkaline treatment, the reaction will have to be conducted under mild alkaline conditions. The extent of cyanoethylation can be determined from the nitrogen content of the material.

Work may be further extended to a study of the reaction mechanism involved in yellowing by comparing the light resistivity of partially acetylated and cyanoethylated fibre with that of the material resulting from the preferential blocking of phenolic OH group.

The working details of the scheme as presented may have to be modified as the work progresses. The broad outline of the scheme may be summarized as follows:

(1) To develop suitable methods for (*i*) acetylation of bleached and raw jute in the liquid phase with minimum discolouration, (*ii*) acetylation in vapour phase, (*iii*) cyanoethylation with minimum adverse effect on fibre and (2) to compare the properties of partially acetylated and cyanoethylated jute. (These properties include tensile strength, moisture affinity and light, heat and rot resistivity).

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Studies in Cellulose Chemistry : Part V— Sodium Metaperiodate Oxidation of Cellulose and Cellobiose

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Cellobiose and cellulose have been oxidized by sodium metaperiodate. Four moles of periodate are consumed per mole of cellobiose to produce 2 moles of formic acid and a substance which is presumably the tetra-aldehyde. Cellulose, on oxidation, loses crystallinity. This has been confirmed by X-ray diffraction study of oxidized cellulose.

The actinic degradation of cellulose has been under study in this laboratory for some time. In the programme of providing reference compounds for understanding the mechanism of actinic degradation, the investigations were extended to the study of metaperiodate oxidation of cellobiose and cellulose. In the meanwhile, Head and Hughes[1] reported that metaperiodate oxidation of cellobiose proceeded continuously until the cellobiose molecule broke down into formic acid, formaldehyde and carbon dioxide as represented by the equation :

$$C_{12}H_{22}O_{11} + 11I\bar{O}_4 \rightarrow 9HCOOH + 2HCHO + CO_2 + 11I\bar{O}_3$$

Earlier, Head[2] oxidized β-methyl cellobioside with sodium metaperiodate and isolated a reducing compound which he regarded as a tetra-aldehyde of methyl cellobioside on the basis of its aldehyde content. By oxidizing cellulose with periodate, Head[3] isolated, among other products, an oxycellulose with a copper number of 102.

The results of controlled oxidation of cellobiose and cellulose with sodium metaperiodate with the object of isolating and characterizing the intermediate products are presented in this paper.

EXPERIMENTAL PROCEDURE

Oxidation of cellobiose

For the study of the rate of reaction, the following method of oxidation was followed: Cellobiose (1 g.) was dissolved in water (300 ml.) and the solution mixed with sodium metaperiodate solution (9.6 g. in 300 ml. water) ; the reaction was allowed to proceed at 20° in a thermostat. A separate experiment was carried out in the dark.

For the isolation of the oxidation product (tetra-aldehyde), the following method[1] was used: Cellobiose (2 g.) was dissolved in water (50 ml.) and mixed with 100 ml. of 6.2 per cent solution of sodium metaperiodate and the mixture made up to 200 ml. The mixture was kept at room temperature (30 C.) in daylight. The reaction was arrested at the Malaprade[5] stage by destroying the excess of periodate or removing it from the sphere of reaction (see methods of isolation and purification) when 4 moles of periodate per mole of cellobiose were consumed. In our experiment this stage was reached at the end of about 90 min.

Rate of oxidation—The rate of oxidation of cellobiose by periodate was followed by determining, at regular intervals (*i*) the amount of periodate consumed and (*ii*) the amount of formic acid produced. Sodium metaperiodate was estimated by the method of Fleury and Lange[6] as described by Jackson[1] and formic acid was estimated by the method described by Head and Hughes[7]. Traces of formaldehyde were detected and estimated by the method of Reeves[8] as adopted by Head and Hughes. The results are graphically represented in Fig. 1.

Oxidation product—Three methods were adopted for isolation and purification of the oxidation product. In the first method (Head[2]), the solution which still contained traces of inorganic materials, was concentrated to dryness under reduced pressure below 50 C. The residue was extracted several times with cold absolute ethanol and the combined ethanol extract on evaporation under reduced pressure yielded a syrup.

In the second method, the excess of metaperiodate in the reaction mixture was destroyed by the addition of the calculated amount of ethylene glycol and the resulting mixture kept aside for a few min. The formaldehyde resulting from the oxidation of ethylene glycol was removed by aeration. The iodine liberated was removed by the addition of a slight excess of sodium thiosulphate solution. The resulting solution was evaporated to dryness under reduced pressure at 45-50 C. and the residue extracted with boiling absolute ethanol (3 × 20 ml.) and the alcoholic extract evaporated under reduced pressure at less than 40 C. A syrup was obtained. This was
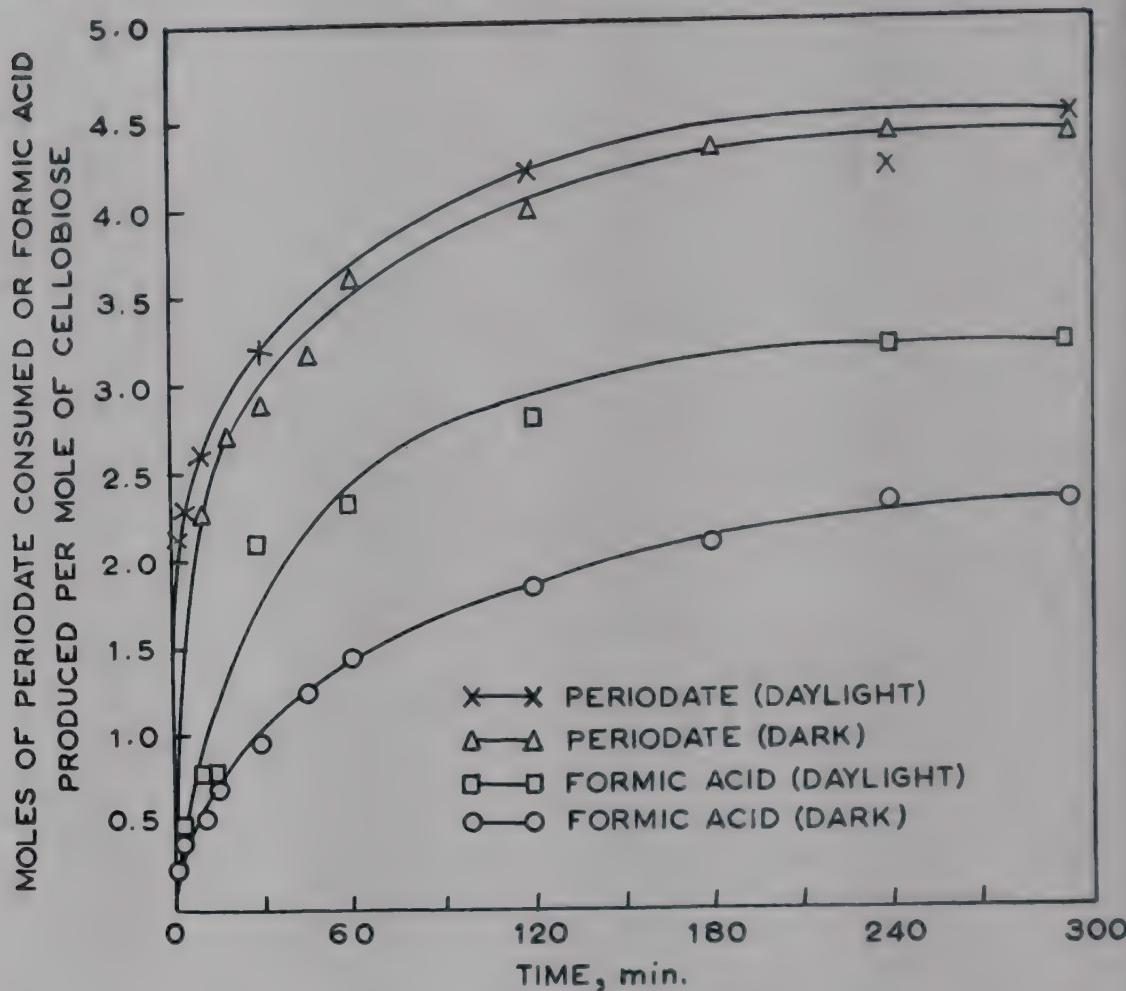
FIG. 1—RATE OF OXIDATION OF CELLOBIOSE BY PERIODATE IN DAY LIGHT AND DARK AS
DETERMINED BY CONSUMPTION OF PERIODATE & FORMATION OF FORMIC ACID

reextracted with boiling absolute ethanol when a small portion remained insoluble. The solution did not undergo any mutarotation in 3 hr ($[\alpha]_D^{30}$ = −2.75°) and showed powerful reducing property.

In the third method, the purification was effected by the use of ion-exchange resins. The solution was first passed through a column (26 cm. long and 2 cm. diam.) of Amberlite IR 120 and then through a second column (22 cm. long and 2.3 cm. diam.) of Amberlite IRA 400. The clear colourless eluate (700 ml.), which was neutral, reduced both Fehling's and Benedict's solutions. It was concentrated to dryness under reduced pressure below 40° C. A white amorphous solid was obtained. As the solid obtained was exceedingly hygroscopic, its m.p. could not be determined.

Preparation of derivatives

Attempts were made to characterize the compound by the preparation of the following derivatives:

2:4-Dinitrophenylhydrazone—The ethanolic solution obtained by the first method was used for the preparation of this derivative. A part of the solution was treated with a solution of 2:4-dinitrophenylhydrazine in dilute hydrochloric acid at room temperature. The orange coloured precipitate obtained was sparingly soluble in benzene and ethanol. Recrystallization of this substance using various solvents was not successful. Its m.p. was found to be above 360°C.

Bromine oxidation[9]—In order to confirm that the oxidation product is a tetra-aldehyde, experiments on further oxidation of the material with bromine were undertaken. For this, the solution obtained by the second method of purification was used. Bromine water (50 ml.) and barium carbonate (3 g.) were added to the solution (concentration of tetra-aldehyde, 12% w/v) and the mixture thoroughly shaken and laid aside in the dark for three days. The excess bromine in the solution was removed by aeration and excess barium carbonate by filtration. To the filtrate, silver carbonate was added to remove dissolved bromide. The resulting mixture was filtered and washed several times with cold water. The filtrate and the washings, after adjusting to pH 7.0, were freed from traces of silver by precipitation with hydrogen sulphide. The excess of hydrogen sulphide was then removed by aeration and the resulting solution was evaporated to dryness at 45-50°C. under reduced pressure, the final drying being effected in vacuum (28-29 in. of Hg) at 45°C. The product obtained was partly crystalline and did not contain any inorganic ion other than barium (Found : Ba, 36.4% ; $C_{10}H_{10}O_{13}Ba_2$ requires Ba, 44.8%).

Attempts to purify the barium salt and to isolate the free tetra acid from both barium and lead salts were made. Barium was precipitated as sulphate and lead, by passing hydrogen sulphide. Attempts to crystallize the acid from the filtrates in either case were not successful.

Oxidation of cellulose

The cellulose used for oxidation was Whatman filter paper No. 1. The oxidation was carried out by the method adopted for the periodate oxidation of starch[4]. The filter paper (0.25 g.) was shredded to bits and kept in contact with a 0.5M aqueous solution (50 ml.) of sodium metaperiodate at 25°C., the mixture being shaken occasionally. After 24 hr, the solution was decanted and the filter paper bits were repeatedly washed with water. Washing was continued until the papers were freed of periodate or iodate ions.

The oxidized paper on drying in air, showed considerable shrinkage. It had a tough horny appearance. It had a very high copper numer (about 100) as against 0.2 for untreated filter paper. Powder photographs of the oxidized material by X-ray diffraction apparatus (North American Phillips)

indicated loss of crystallinity.   Davidson[10] has reported that periodic acid oxidation of cellulose destroys the original crystalline order of the cellulose.

DISCUSSION

The oxidation of cellobiose by periodate takes place very rapidly during the first hour in daylight ; subsequently it slows down.   When the oxidation is carried out in the dark, the rate of oxidation is slower (Fig. 1).   After 90 min. of reaction in the daylight, about 4 moles of periodate are consumed. The theoretical amount of periodate consumed for the Malaprade stage is 4 moles/mole of cellobiose with the production of 2 moles of formic acid.

As the product obtained by oxidation had high reducing property and as it was possible to prepare the impure barium salt by further oxidation with bromine, it may be presumed to be a tetra-aldehyde.   However, the inability to prepare the 2 : 4-dinitrophenylhydrazone in the pure state may be due to the presence of interfering impurities in the periodate oxidation product.

SUMMARY

Cellobiose on oxidation with sodium metaperiodate produced a compound with reducing property, presumably the corresponding tetra-aldehyde.   This was obtained as an amorphous solid free from ionic impurities.   Four moles of periodate are consumed in 90 min. when the oxidation takes place in daylight and in 120 min. when the oxidation is carried out in the dark ; 2.6 moles and 1.8 moles of formic acid are produced by the reactions in daylight and in the dark respectively.   Treatment of the oxidation product with 2 : 4-dinitrophenylhydrazine did not yield any well defined derivative. Oxidation with bromine water in the presence of barium carbonate yielded a semicrystalline barium compound.   Periodate oxidation of Whatman filter paper No. 1 (cellulose) resulted in the loss of crystallinity of the cellulose molecule with the formation of a tough, horny substance with copper number c. 100.

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Fundamental Study in Tone and Shade Control in Continouus Dyeing of Cellulosic Textiles at Elevated Temperature

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"Dyeing is an old industry and development in it for a long time came only slowly ; until in fact Perkin synthesized Mauve . . . . It was really the advent of new (synthetic) fibres which demonstrated the need for new dyeing techniques. It was only when grave difficulties were experienced in dyeing a new fibre with established dyestuffs and techniques, that new techniques were evolved . . . . New dyeing processes were, therefore, forthcoming to meet the special demands of new fibres, but when once the new processes had been developed, their use was extended to natural fibres too and often with beneficial results."[1] These new dyeing processes envisage continuous operation at elevated temperatures.

Steps in continuous dyeing—Continuous dyeing of textiles consists of the following steps: (*i*) Passage of the fabric through the dye solution or dispersion (liquid treatment) ; (*ii*) padding to obtain uniform distribution ; and (*iii*) heat treatment to obtain diffusion and fixation or chemical reaction of the dye molecules with the fibre substance at localized sites in a short time.

Each of these steps is a technique by itself requiring efficient control, since it is difficult to rectify the mistakes at the subsequent step. Hence it is needless to stress the importance of the factors that are responsible for the efficiency of each of these steps in obtaining well-penetrated, uniform solid shades without any adverse effect on the tone of dyeing.

Liquid treatment—The passage of cloth through the dye solution or dispersion should enable it to absorb enough solution so that thorough wetting takes place and the dye solution penetrates the fabric completely.

However, in the continuous method of dyeing, the following restrictions are imposed, on which a compromise must be reached for the process to be economical as well as efficient: (i) The time of contact with the dye liquor is of the order of a fraction of a second. For example, in the Standfast Molten Metal Unit, the contact time is 0.44 sec. at 30 yd per min. and 0.11 sec. at 120 yd per min. (ii) The volume of dye bath must be as small as possible in order that there is minimum wastage of dye liquor at the end of the run. (The dye bath of the Standfast Molten Metal Unit is the smallest known in continuous dyeing operations.) (iii) The concentration of the dye solution should be much higher than that normally used. (iv) The affinity of the dyestuffs for the material produces what is known as tailing effect. (v) The dye bath temperature should be as high as possible so that the time required during the heat treatment of material is reduced to a minimum. (vi) The rate of feed must match the rate of pick-up of the dye solution by the material in order to reach (dynamic) equilibrium as early as possible. (vii) The feed liquor should not be far different in concentration from the dye bath solution ; in fact, it would be preferred if the feed liquor is of the same concentration as the dye bath solution at the start.

The study of these factors with respect to dye bath construction forms an important aspect of the continuous dyeing technique for obtaining uniform shades with minimum tailing effect.

Tailing effect arises on account of the affinity of the dye for the fibre, whereby the amount of dye uptake by the fibre is always in excess of that given by the squeeze per cent. As a result of this, the concentration in the fabric suffers corresponding variation in colour. At the equilibrium stage the excess amount of dye taken up by the fabric equals the difference between the added dye and the dye in the trough, so that the fabric gets a continuous and uniform shade. The problem of tailing is related to the time required for the padding system to come to an equilibrium, or in other words, the length of cloth which must be run before a uniform colour is obtained. Table 1 illustrates this point.

The yardage required to ensure consistency of depth (within 5%) can be calculated by taking into consideration the affinity factor, dye bath capacity and rate of feed.

The affinity factor itself is a complex entity depending on a number of factors besides the intrinsic character of the dye molecule itself, e.g. concentration, temperature of the dye bath, presence of salt and other compounds in the dye bath, fabric construction and fibre properties, and padding system.

There appears to be no systematic study of each of these aspects independently. Adequate details of the work done so far are not available. Some

TABLE 1—YARDAGE OF DIFFERENT FABRICS UNDER VARYING TROUGH
CAPACITIES AND MANGLE EXPRESSION

FABRIC	MANGLE EXPRESSION %	YARDAGE FOR PAD THROUGH CAPACITIES OF		
		40 gal.	10 gal.	2 gal.
4 oz. Poplin	50	5,000	1,200	240
8 oz. Cotton twill	60	2,000	500	100
	100	1,200	300	60
	150	. .	. .	40
12 oz. Duck	100	800	200	40

information is available with respect to the Standfast Molten Metal Unit[2] where the feed liquor and agitation in the bath stimulate horizontal as well as vertical movement of liquor on both sides of the cloth. Recently, the idea of high turbulence in a small narrow dye bath through jets has been introduced[3] to overcome the difficulty of tailing in continuous ribbon dyeing. Bond's machine[4,5] utilizes jets of hot dye solution to obtain complete dyeing. The latest innovation in dye bath construction is the application of ultrasonics[6-8] to obtain adequate mass transfer and penetration. This, however, is still of academic interest. Recently, the authors have applied the technique of fluidized beds of solid discrete particles where the dye solution acts as the fluidizing medium[9] (Fig. 1).

In addition to the homogeneity of dye bath liquor and fabric penetration, which are obtained satisfactorily by adopting a few of the methods, there are other factors, such as properties of high concentrated dye solutions, dye bath capacity, rate of feed affinity and strike of the dye and fabric construction, which demand attention. All these contribute to the tailing effect, i.e. the differential shade obtained in the beginning and at the end. Mann[10] and Marshall[11] have carried out a fundamental study of these factors and suggested means of reducing the tailing effect. One of the suggestions pertains to the dye bath capacity and the rate of feed. According to them, the trough capacity should be as low as possible so that the cloth empties it many times, at least one and a half-times, within a short time.

It is, therefore, evident that the control of shade in a continuous dyeing system is a complex problem requiring considerable skill and knowledge on the part of the dyer. This complication would be all the more aggravated when a mixture of dyes is to be applied to the fabrics. In order to understand this complex system in which a number of variables are involved, it is necessary to study the affinity factor under various sets of conditions that are normally encountered and evaluate their relationship with other variable factors involved.
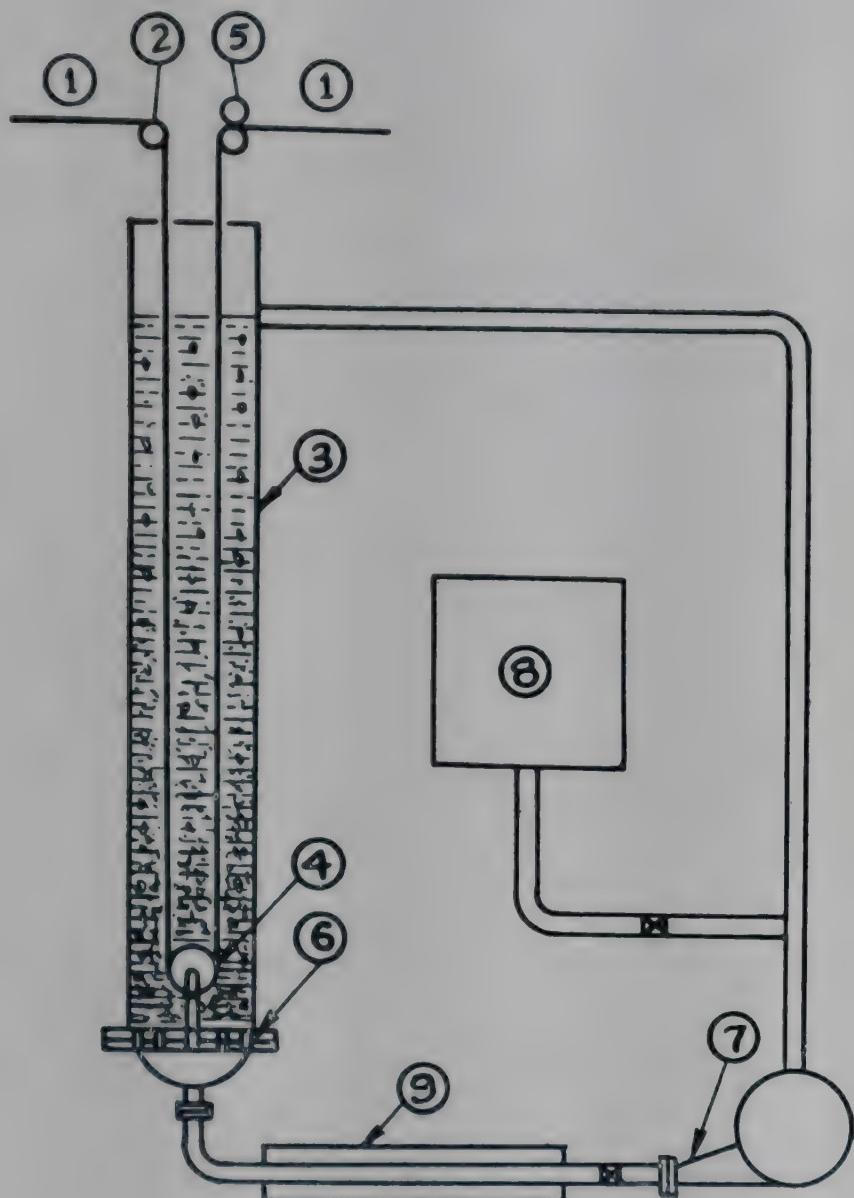
FIG. 1—LIQUID FLUIDIZATION UNIT [(1) Cloth, (2) Guide roller, (3) Liquid fluidization column, (4) Porous guide roller, (5) Draw rollers, (6) Distribution plate, (7) Circulation pump, (8) Storage tank and (9) Heat exchanger]

Padding—The cloth passes through the liquid first and then through the padding mangle to obtain the requisite squeeze per cent and uniform distribution of the dye along the length and the width of the fabric. Hence, uniformity of shade depends on the efficiency of the padding mangle, particularly in a system of continuous dyeing not involving subsequent levelling off of the dye. It is only recently that the padding mangle and the padding system have received attention from the fundamental point of view[12,13]. It has already been pointed out that the padding mangle also plays an important part in the tailing effect by controlling the liquor pick-up on which dye feed depends.

Heat treatment—The dye molecules which have been transferred to the requisite sites or close to the requisite sites are fixed *in situ* finally by heat

treatment. Methods of heat treatment for the fixation of dye molecules on the fibre have considerably improved since the advent of synthetic fibres, which normally require high temperatures. Molten metal, hot oil, steaming chambers, hot flues, infra-red heating and, more recently fluidized beds[2,14-16] (Fig. 2) are some of the methods of heat treatment. These developments have been essentially intended to meet the special demands of synthetics which are employed, mainly, as dispersed dyes. The dyes have no affinity for the fibre and are supposed to form solid solution with the fibre material. In adopting these techniques for natural fibres[16], a number of problems are to be faced, such as stability and behaviour of natural fibres at high temperatures, stability and behaviour of dyestuffs at high temperatures, high rates of diffusion of dyestuffs at high temperatures, and moisture versus migration of dyestuff molecules into the fibre substance.

On account of the high rates of diffusion[17-19] at elevated temperatures, the actual time of heat treatment is considerably reduced ; for example, for vats in pad steam process it is about 15-25 sec. and for directs, 2 to 3 min.[20] ; in the Standfast Molten Metal Unit, it is 1.6-7 sec. In the fluidized bed technique developed in the *Shri Ram Institute for Industrial Research*, the authors have found that heat treatment for 3 to 8 sec. (even 1 to 3 sec.) is sufficient to obtain satisfactory dyeing. In all these cases, particularly when the temperature exceeds 120-130°C., the dyeings suffer from tone change as compared to normal dyeing. Tone changes are due to decomposition or structural changes in dye molecules, e.g. possible over-reduction in the case of leuco-vat dyes or reduction of directs in the presence of cellulose
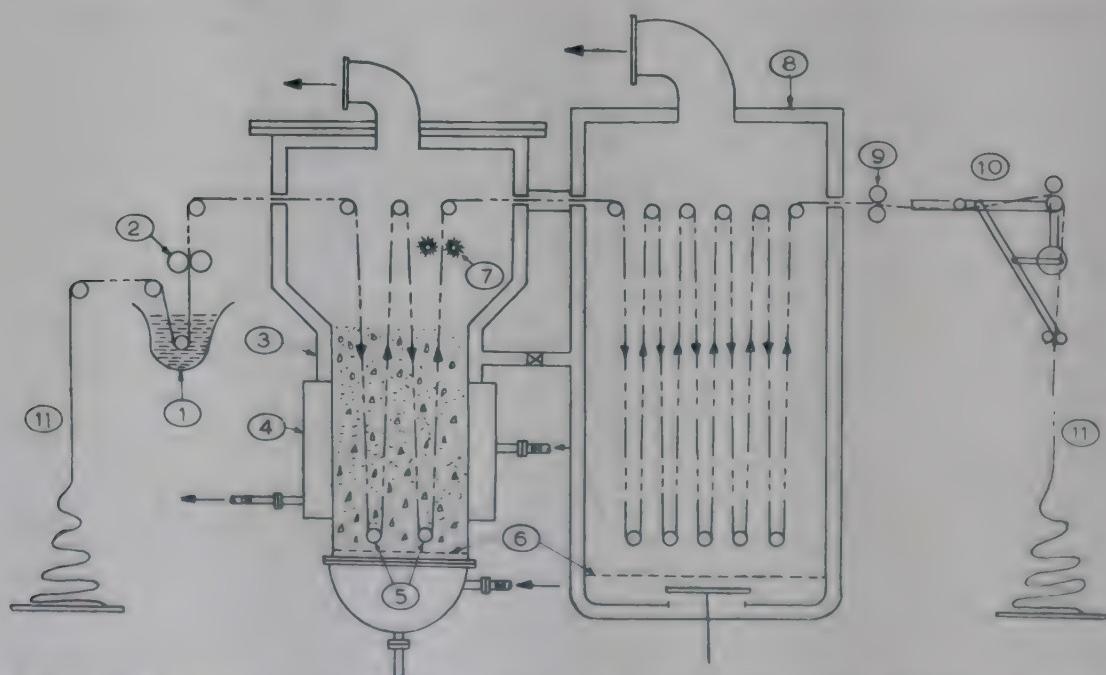

Fig. 2—FLUIDIZED BED DYEING UNIT [(1) Dye bath, (2) Padding mangle, (3) Fluidized Bed Unit, (4) Steam jacketing, (5) Porous guide rollers, (6) Distribution plates, (7) Brushes, (8) Steaming chamber, (9) Draw rollers, (10) Collecting arrangement and (11) Cloth]

and alkali[21-23]. In fact, at present, manufacturers of dyestuffs supply a classified lists of temperature stable dyestuffs for the use of dyers ; however, the lists cannot be used to the fullest advantage where conditions are not identical with those recommended by manufacturers. It appears that the tone can be controlled, to a certain extent, by properly controlling moisture and by using protective agents, such as hydrogen peroxide, sodium percarbonate, perborate and dichromate. These agents, however, are not useful above 100°C. ; further they increase the alkalinity of the material after decomposition. Ammonium salts of mineral acids are somewhat better, but not altogether satisfactory. The addition of monochrom mordants gives better results than all the protective agents recommended so far[21].

In the case of vat dyes, the problem is two-fold, namely prevention of over-reduction of the lecuovat and also arresting premature decomposition of the reducing agent, e.g. hydrosulphite. In order to prevent over-reduction, the use of dextrin, inorganic nitrites, hydroxylamines, etc. has been suggested and some measure of success has been reported.

CONCLUSION

The fundamental study of the subject involves a two-fold attack ; firstly, dye bath construction which should take into account a number of mechanical aspects, and secondly, chemical aspects pertaining to the dyestuffs employed. The problem is complicated in the case of cellulosic fibres on account of the complex mechanism of dye-sorption.

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Application of Fluidized Beds to Textile Processing

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Theoretical aspects of fluidized bed technique are discussed. The application of fluidized bed technique to textile processing and problems involved in its application are analysed with particular reference to the effect of passage of textile fabric on the pattern of fluidization and the effect of fluidization on the passage of fabric.

The technique of fluidization, though known for the last fifty years or so, excited industrial interest only recently[1]. It was first introduced in the petroleum industry during World War II. The inherent advantages of this technique are: (*i*) exposure of a large specific surface for the reaction ; (*ii*) high thermal conductivity of the reaction surface[2,3] ; (*iii*) excellent control and uniformity of temperature[2] ; and (*iv*) high overall heat-transfer coefficient[1]. These advantages have made this technique applicable in many commercial operations, such as roasting of gold ores, calcination of limestone, manufacture of carbon black, phthalic anhydride, hydrocarbons and chemical synthesis from hydrogen and carbon monoxide[2], catalytic dehydration and dehydrochlorination[4], selective diffusion of gases[5], etc. ; it is also reported to be applicable to the reduction of iron ores[2] and manufacture of cement.

Of late, this technique has attracted the attention of textile technologists as well. For the last three years, the *British Rayon Research Association* in U.K.[6], and the *Shri Ram Institute for Industrial Research* in India[7] have taken up the development of this technique for textile processing.

BED CHARACTERISTICS

When a fluid is caused to flow upward through a bed of suitably sized solid particles at a velocity sufficiently high to buoy the particles and to impart to them a violently turbulent motion, the bed exhibits characteristics similar to those normally associated with fluids, such as, mobility and hydrostatic

pressure[2,3], and hence this bed is called Fluid Bed or Fluidized Bed ; the technique is known as Fluidization.

The effects of different variables on some of the characteristics of the bed are discussed below :

Velocity of fluidizing medium—The relation between velocity of the upward flow of gases and the pattern of fluidization and also the pressure drop of the upward flow of gases are shown in Fig. 1 & 2.

Fig. 1*a* represents a vertical pipe containing a fixed bed of solid discrete particles supported on a grid, a stream of gas entering below the grid and passing upward through the bed and two pressure taps P_1 and P_2 located about the middle of the packed height and at a distance of L.   Fig. 2 shows graphically, in the logarithmic scale, the relation between superficial upward gas velocity and $(P_1 - P_2)/L$.

On increasing the velocity of upward flowing gas gradually from zero, the gas passes through the voidage in the bed without any movement of the solid particles ; this is represented by curve OA in Fig. 2.   On increasing the velocity of gas, there is a slight expansion of the bed and readjustment of particles so that the bed attains the loosest stable configuration (Fig. 1*b*) ; this is represented by curve AB.   At point B, $(P_1 - P_2)/L$ has reached a value equal to the weight of solids per unit tube cross-section between the taps P_1 and P_2.   The condition at B is known as dense homogeneous phase or incipient fluidization.

On further increasing the velocity of gas, a part of the gas flows through a denser but expanded bed which constitutes a continuous phase while the balance of the gas passes through the bed in the form of bubbles which constitute a discontinuous phase (Fig. 1*c*).   Now the solids are violently agitated ; this condition may be termed as turbulent or two-phase fluidization,
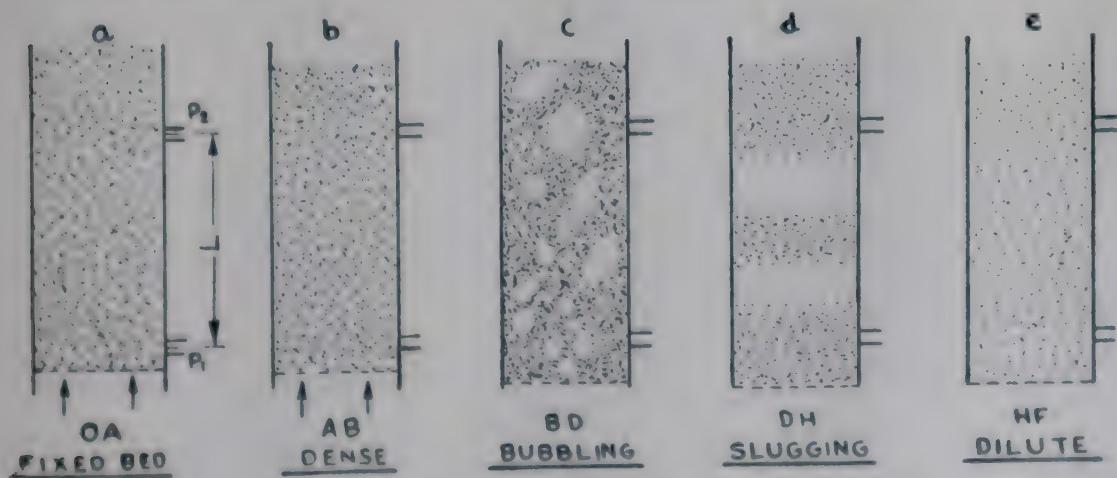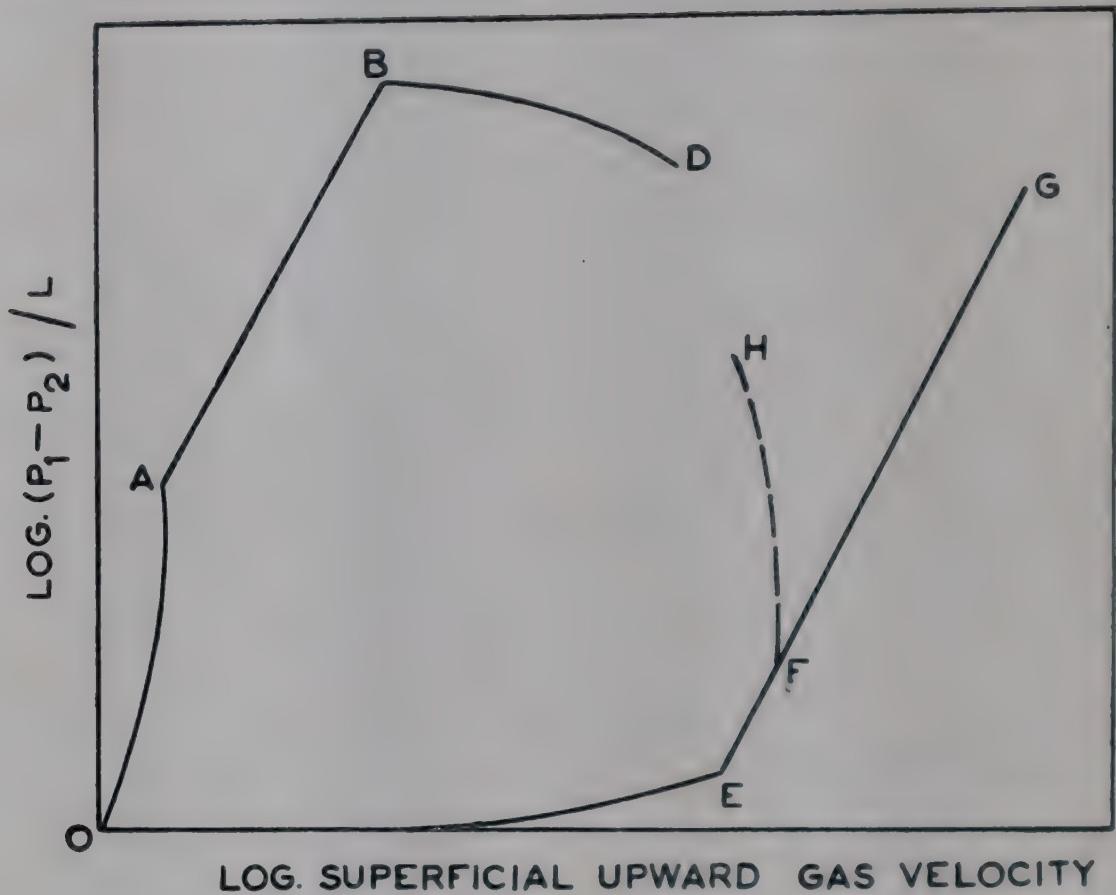

FIG. 1—PATTERN OF FLUIDIZATION

FIG. 2—PRESSURE DROP VERSUS UPWARDS GAS VELOCITY

which is represented by curve BD. At point D the number and size of bubbles increase and as a result a number of them coalesce and grow to a size equal to that of the tube before escaping from the bed and this creates gas pockets pushing short columns or slugs of solid particles up the tube. Every few seconds a bubble will burst through the top of the tube. This is termed as slugging (Fig. 1d).

On increasing the velocity still further, a disperse or dilute homogeneous phase fluidization results (Fig. 1e) which is represented by the curve HF. Point F at which only one particle remains, represents the balancing velocity for a single particle or that of the largest particle in any mixture and falls on the curve $OEFG$ which represents the pressure drop for the flow of gas alone through the empty tube.

Heat transfer coefficient—The overall heat transfer coefficient in a fluidized bed is higher than that in a packed bed and far higher (40-100 times) than that in a gas convection system on account of the reasons given below:

The heat transfer coefficient in the fluidized bed is not affected by the thermal conductivity of the solid particles constituting the bed (the thermal conductivity of the bed is about 100 times that of silver[*]). The heat transfer

coefficient increases gradually with increase in the mass rate of gas flow till the bed starts slugging (corresponding to the point D in Fig. 2). On further increase in mass rate of gas flow, there is a steep fall in the heat transfer coefficient (sometimes as much as 50%). The effect of mass rate of gas flow is shown in Fig. 3.

The effects of particle diameter and solid concentration or bulk density of the bed are also shown in Fig. 3. The smaller the particle diameter, the higher is the heat transfer coefficient. With increase in solid concentration, the heat transfer coefficient gradually increases, reaches a maximum and gradually falls down.

Slugging—As the heat transfer coefficient in the fluidized bed is considerably reduced (to the extent of 50%) by slugging conditions in the bed, it is important to consider the effects of different variables on slugging conditions.
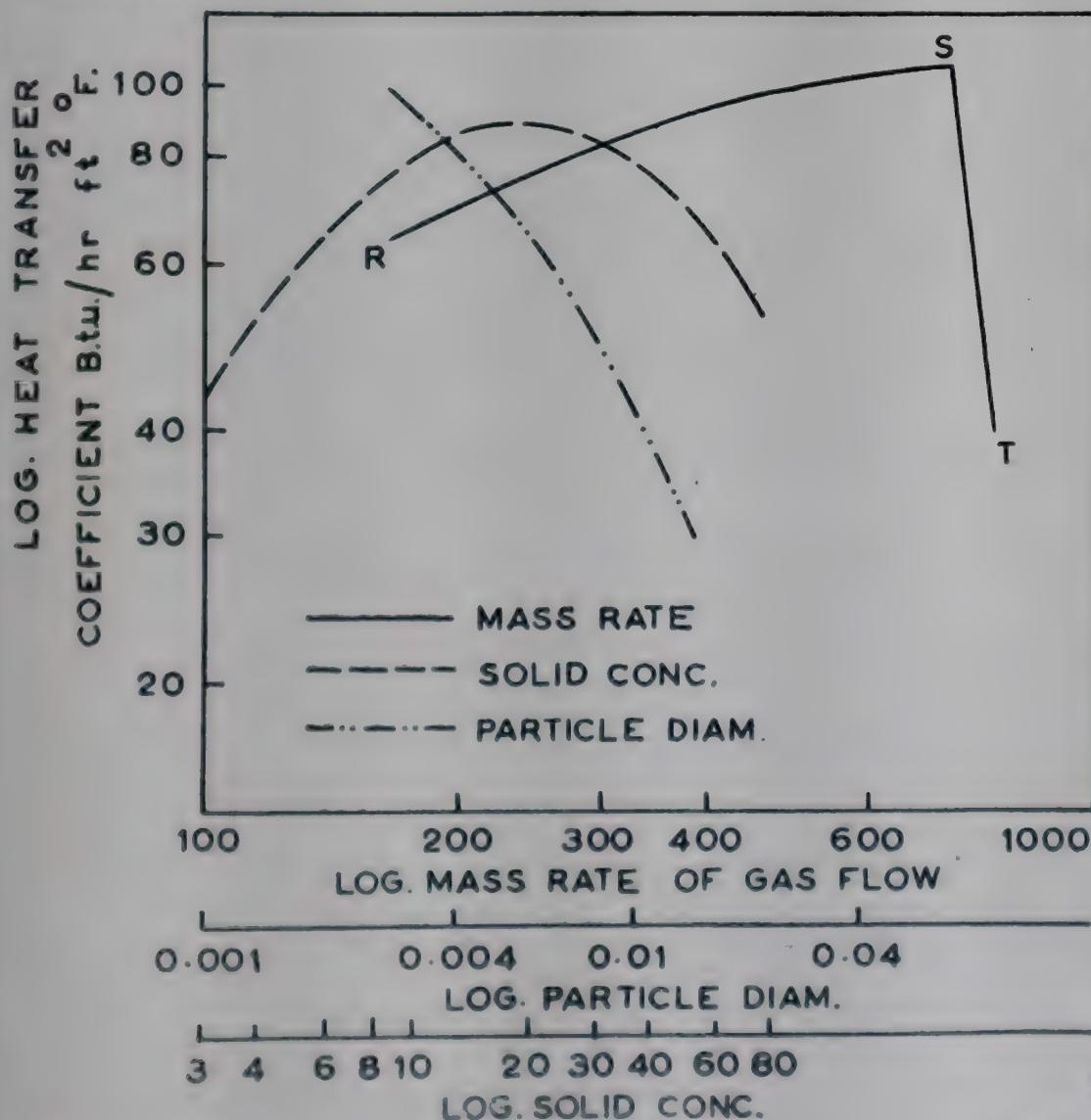

FIG. 3—EFFECTS OF MASS RATE OF GAS FLOW, PARTICLE DIAMETER AND SOLID CONCEN-
TRATION ON HEAT TRANSFER COEFFICIENT

The effect of diameter of the solid particles constituting the bed and the ratio of density of the particles to that of the fluidizing medium are shown in Fig. 4, wherein curves DP_1 and DP_2 represent the bed density versus ratio of particles density to fluid density of the bed of particle sizes DP_1 and DP_2. At low ratio of particle density/fluid density, ρ_s/ρ_f (corresponding to P), the bed of particle size DP_1 will fluidize without slugging, while the bed of particle size DP_2 will slug between bed voidages of A and A', while the bed of particle size DP_1, will fluidize with slugging at ρ_s/ρ_f represented by Q between bed voidages B and B'.

The effect of increasing the height/diameter ratio of the bed is similar to that of increasing the diameter of particles constituting the bed. The higher this ratio the wider is the range of bed voidage during which slugging occurs, and the lower is the heat transfer coefficient.

It has been found that the dimensionless group $D_p L_f/A$ or (particle diam. × bed height)/(cross-sectional area of bed) defines the transition from the flow (Type 2) in the ordinary fluidized bed to that (Type 1) in the slugging bed, the transition value being 0.008. In Fig. 5, Type 1 curve corresponds to $D_p L_f/A > 0.008$, where the heat transfer coefficient decreases as the height increases ; and Type 2 curve corresponds to $D_p L_f/A < 0.008$, where the heat transfer coefficient increases to a maximum and then falls down with increase in bed height. From the relationship $D_p L_f/A$ it is clear
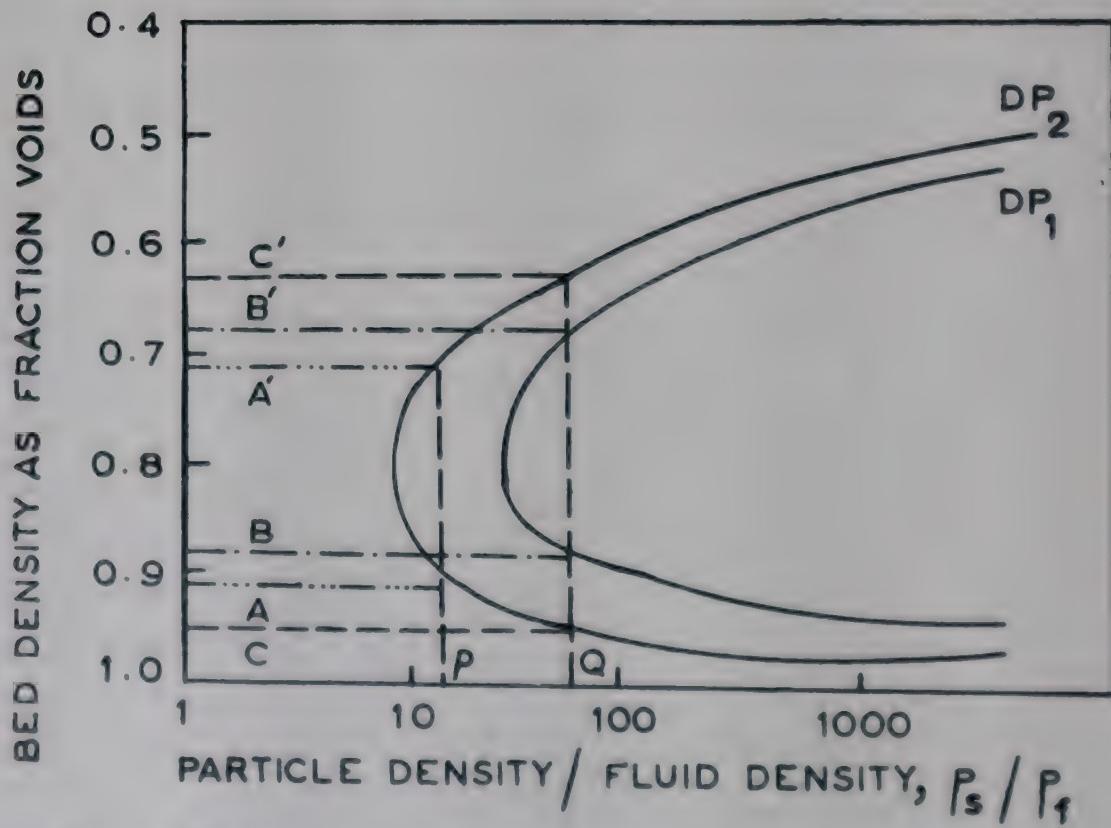

FIG. 4—BED DENSITY VERSUS RATIO OF PARTICLE DENSITY TO FLUID DENSITY
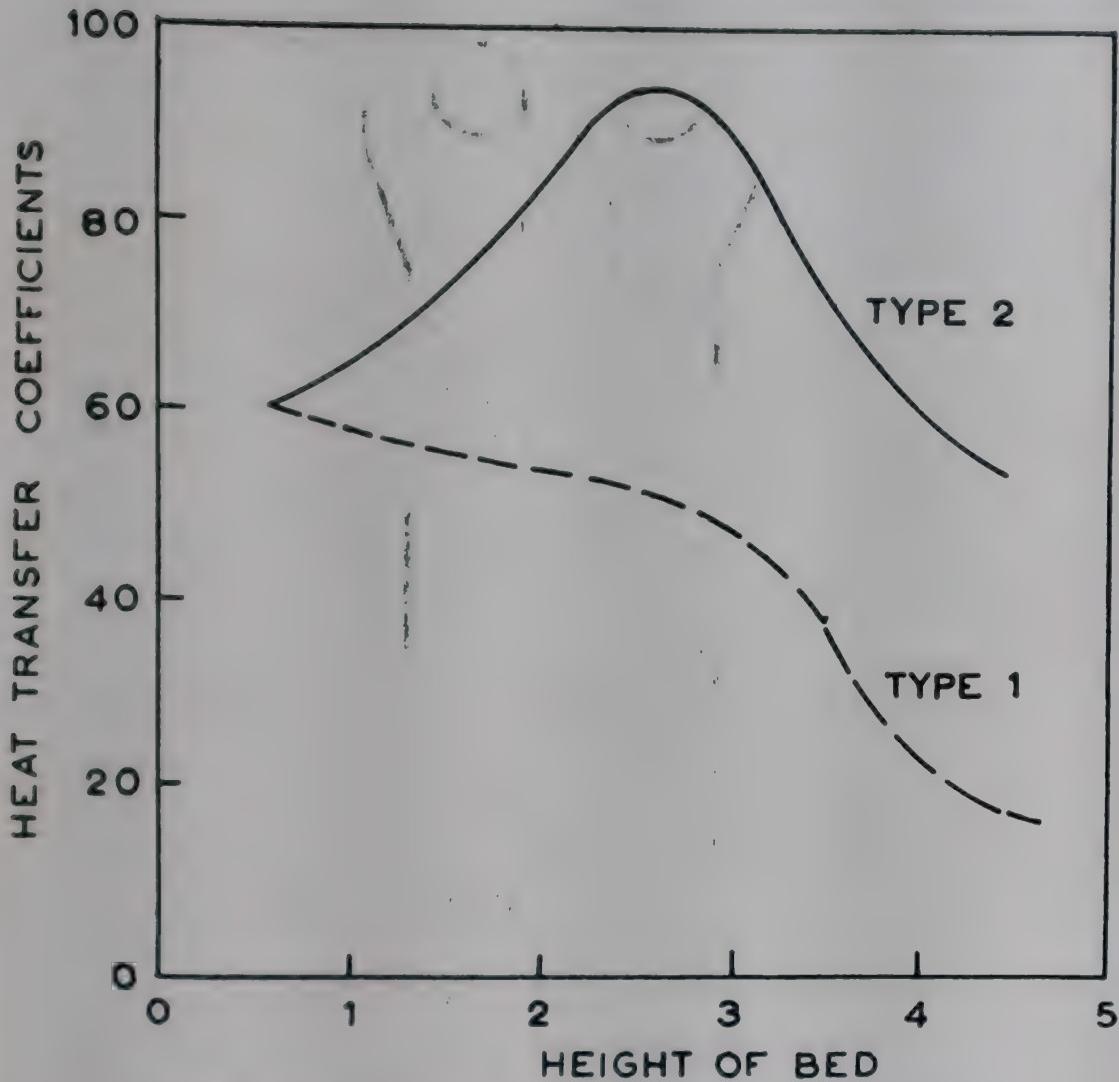
FIG. 5—HEAT TRANSFER COEFFICIENT VERSUS HEIGHT OF BED

that the higher the ratio of height to cross-section of the bed and greater the particle diameter, the greater is the slugging tendency.

APPLICATION TO TEXTILE PROCESSING

This technique of fluidization can be used for both dry processing of textiles, such as curing of resin-treated textiles and heat setting of synthetic fabrics, and wet processing of textiles[9], such as dyeing and, perhaps, scouring and bleaching. In all these processes the uniformity of temperature, the high heat transfer coefficient and the high thermal conductivity of the bed could be advantageously utilized. The efficiency of the fluidized bed as a heat transfer medium can be ascertained indirectly from Table 1 which shows the amount of steam required to evaporate 1 lb. of water from the fabric in common fabric-drying systems and that in the fluidized bed : it is clear from the Table that the efficiency of fluidized bed equals the most efficient drying system (cylinder drying).
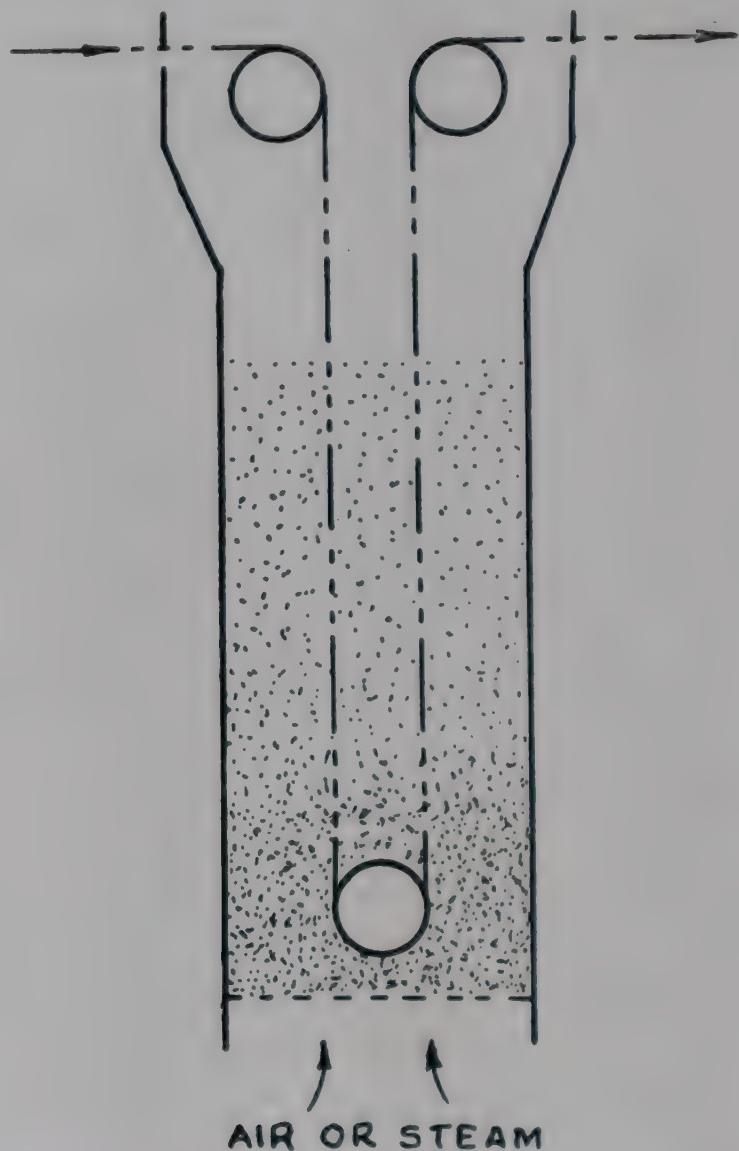
Application of this technique to textile processing appears simple, but there are many practical considerations involved in the application. Some of them are discussed below:

Guiding the fabric through the bed—The solid discrete particles constituting the bed may enter the bearings of fabric guide rollers embedded in the bed and cause either partial or complete stoppage of the roller which, in turn, might cause tension in the fabric to such an extent that the fabric may tear or even break.

Pattern of fluidization—The fabric moving through the fluidized bed will stir the bed to some extent and this will help in using a lower velocity of gas for fluidization. Roland Beck has shown that when stirrers are used in a fluidized bed, a lower velocity of the fluidizing medium gives satisfactory

TABLE 1—STEAM REQUIRED TO EVAPORATE 1 lb. OF WATER FROM
FABRIC IN FABRIC-DRYING UNITS

Unit	Steam lb.
Drying cylinders	1.5
Stenter (conventional)	2.5
Stenter (High velocity jets arranged close to fabric)	1.6
Fluidized bed	1.4

fluidization. As pointed out earlier, a lower velocity of gas reduces the chance of slugging and also increases fluidization efficiency. This moving fabric might break the slugs of solid particles moving through the column.

On the other hand, the passage of fabric through the fluidized bed of solid discrete particles divides the bed into different portions longitudinally, thus increasing in effect the height/diameter ratio. The result will be that the flow pattern will be similar to that of type 1 shown in Fig. 5 and the heat transfer coefficient will be lowered.

Effect on the fabric—The fabric moves through the bed more or less vertically and as the bed of solid discrete particles is completely buoyed by the upward flowing gases, there will not be any side thrust on the fabric as would be expected in a fixed bed. This is proved by the fact that the force required for running the fabric through a fixed bed is far higher than that for running the fabric through a fluidized bed. But as there is also violent agitation of particles, the particles will strike the moving fabric which may cause it to move from its straight path ; either the folds of the fabric balloon out and touch the walls of the unit or the folds come close together. The fabric may flutter. These movements of the fabric cause undue tension ; the fabric may fold at its ends or creases may be formed. These introduce non-uniformity of treatment in certain cases ; and in certain other cases, curing, creasing and folding by themselves are undesirable.

Particles carried over by the fabric—The fabric leaving the fluidized bed carries with it a lot of solid discrete particles ; this trouble is much more in the wet processing of textiles and still more when the particles are fine. There is a gradual depletion of the bed. In addition, the solid particles sticking to the fabric may spoil the fabric draw rollers and also the fabric to some extent.

CONCLUSION

The successful application of fluidization technique will depend on the satisfactory solution of the various problems discussed in this paper. Some of the problems, e.g. design and construction of the bottom guide roller[10] and carry over of solid particles with the fabric, have been solved by the authors.

ACKNOWLEDGMENT

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Studies on the Chlorine Retention of Resin-Treated Cellulosic Fibres

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Thermosetting resins are commonly used for the finishing of cotton fabrics so as to impart to the cotton fibre some of the desirable properties of synthetic fibres, such as low moisture absorption, dimensional stability and increased elasticity. One of the serious problems associated with the use of resins is the retention of chlorine when the fibre is treated in hypochlorite baths for laundering. The retained chlorine produces severe degradation of the fabric on subsequent ironing.

It has been generally assumed[1-3] that chlorine reacts with R_2NH groups in the resin polymer to form chloramines, R_2NCl, which, at the high temperatures used in ironing, liberate hydrogen chloride leading to cellulose degradation. Urea formaldehyde (UF) and melamine formaldehyde (MF) resins are thus classed as chlorine retentive, because in the resin polymers formed from dimethylolurea and methylolmelamine, R_2NH groups are expected to be present. In fact, cotton or viscose treated with these resins under usual conditions of polymerization do show a high degree of chlorine retention and loss of tensile strength. On the other hand, the newer types of resins, such as trimethylmethylolmelamine and dimethylolethyleneurea (DMEU) are supposed to react with cellulose hydroxyls. Cross linking is a more dominant reaction with these resins than polymerization and the final product does not have any R_2NH groups. These resins are classed as non-chlorine retentive. The purpose of this paper is to present some data to show that: (i) it is not correct to group resins as chlorine retentive and non-chlorine retentive ; (ii) under certain conditions of polymerization, even the so-called chlorine retentive resins may show very little retention of chlorine ; (iii) conversely, under certain conditions of polymerization, the so-called non-chlorine retentive resins may show very high chlorine retention ; and (iv) the accepted mechanism of chlorine retention and damage through chloramine formation may not give the complete picture.

Table 1 shows the extent of chlorine retention by cotton treated with different resins polymerized under the usual conditions of processing.   It can be seen that the last two products show substantially lower chlorine damage than the first four.   However, the data in Table 2 show that even with un-modified UF and MF resins, chlorine retention damage decreases significantly as the amount of resin in the cotton fibre is increased.   It is possible that with increasing concentration of resin, the building up of the 3-dimensional polymer takes place to a larger extent, making a smaller number of R_2NH groups available for reaction with chlorine.   It may also be that with increasing amounts of resin, decreasing inhibition of aqueous reagents and perhaps slower rates of diffusion play a part.   In any case, this behaviour which has been consistently observed needs an explanation.

TABLE 1—CHLORINE RETENTION DAMAGE WITH DIFFERENT RESINS

RESIN	CREASE RECOVERY WARP & FILLING	TESNILE STRENGTH LOSS, %
Urea formaldehyde	240	85.15
Melamine formaldehyde	252	69.53
Modified urea formaldehyde	268	86.28
Urea formaldehyde	243	91.87
Methylated melamine formaldehyde	239	23.74
Dimethylol ethylene urea	257	19.16

TABLE 2—EFFECT OF THE QUANTITY OF RESIN ON CHLORINE RETENTION DAMAGE

RESIN	CONCENTRATION	TENSILE STRENGTH LOSS, %
Urea formaldehyde	A	90
	B	75
	C	56
	D	48
Melamine formaldehyde	A	90
	B	82
	C	51
	D	28
Urea formaldehyde	A	91
	B	89
	C	70
	D	62
Modified urea formaldehyde	A	93
	B	85
	C	74
	D	37

TABLE 3—EFFECT OF PROCESSING CONDITIONS ON CHLORINE RETENTION DAMAGE

RESIN	FABRIC ALKALINITY % NaOH	CATALYST moles/l.	CURE temp. °C.	CREASE RECOVERY	TENSILE STRENGTH LOSS, %
Melamine formaldehyde	0.06	AMP (0.06)	140 180	2.8 3.2	85 5
		MgCl₂ (0.06)	140 180	2.8 3.3	95 0
	0.30	AMP (0.06)	140 180	2.2 2.8	100 100
		MgCl₂ (0.06)	140 180	2.5 3.1	100 15
		AMP (0.12)	180	3.3	0
		MgCl₂ (0.12)	180	3.4	0
Dimethylol ethylene urea	0.15	MgCl₂ (0.036)	140	2.8	65
	0.30	AMP (0.072)	160	2.8	80

Even more striking are the differences in chlorine retention and damage observed with the same resin when polymerized under different conditions. Table 3 shows some published data[1], which have been substantially corroborated in our laboratory. It is obvious that depending on fabric alkalinity, catalyst concentration and curing temperature, damage due to retained chlorine can vary, for a so-called chlorine retentive resin, from 0 to 100 per cent. Similarly, even a so-called non-chlorine retentive resin, such as DMEU can give, under certain processing conditions, chlorine retention damage of 65 to 80 per cent. It was pointed out earlier that a substance such as DMEU would tend to cross link cellulose rather than form a polymer inside the fibre. In that case, the mechanism of chlorine retention by such a resin is likely to be different from the formation of chloramine.

In short, the problem of chlorine retention by cellulose treated with different resins appears to be more complicated than it has been assumed to be so far. It is necessary to study this reaction in greater detail to see whether : (i) the reaction of chlorine with cotton or viscose treated with a given resin under given conditions is stoichiometric or is dependent on the conditions of chlorine treatment : (ii) diffusion and accessibility play any part in chlorine retention : (iii) R_2NH groups can be estimated independently and correlated with the extent of chlorine retention : and (iv) the wide variation in chlorine retention by the same resin polymerized under different processing conditions is due to differences in the amount of R_2NH groups or to differences in accessibility.

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Studies in the Fluidity of Cellulose Solutions. K. N. GUPTA, J. VERGHEESE, H. R. CHIPALKATTI & V. B. CHIPALKATTI (Shri Ram Institute for Industrial Research, Delhi).

A study of viscosity behaviour of cotton cellulose (in 85%) phosphoric acid has been made and zero time intrinsic viscosity values calculated. It is postulated that zero time intrinsic viscosity is related to miceller packing and size rather than to the degree of polymerization (D.P.). In order to examine this, a number of samples of cellulose treated under various conditions have been examined. These treatments include acid and alkali swelling, hydrolysis, oxidation, etc.

This study indicates that the parameters of the function of intrinsic viscosity with time are significant properties of dissolving entity. However, their quantitative aspect is not very clear and is being further pursued. The sensitivity of this function is particularly to be noted when new linkages are produced in the polymer structure either through stretching or formalization or intensive hydrolysis. The programme of future work is briefly discussed. (*Abstract*)

Acid Polymerization of Furfural and 5-Hydroxymethylfurfural. P. K.
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Science and Technology, Calcutta).

Furfural and 5-hydroxymethylfurfural (HMF) polymerize in acid solution
forming initially a linear polymer which rapidly becomes cross-linked. This
cross-linking is strongly catalyzed by mineral acids, like hydrochloric and
sulphuric, which prevent systematic study of their reaction mechanism.
However, polymerization in phosphoric acid solution is slow and gradual,
and this has been studied by light scattering and viscometry.

Attempts are being made to isolate the linear polymer from phosphoric acid
solution with a view to preparing thermosetting moulded articles from furfural
and HMF resins. (*Abstract*)

High Alpha-Cellulose Pulps for Viscose Rayon from Indian Cellulosic Materials

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High alpha-cellulose pulps have been prepared from five indigenous
cellulosic materials (wattle, blue gum, *muli* bamboo, *daba* bamboo and
sugarcane bagasse) using water-prehydrolysis sulphate process and suit-
able multi-stage bleaching process. The pulps are chemically pure but
their viscose filterability has to be evaluated before their suitability for
the manufacture of viscose rayon can be confirmed.

There are four plants manufacturing viscose rayon in the country ; one of
them produces transparent paper also. The requirements of viscose rayon
pulp in the Second Plan period has been estimated at 51 million kg.
Although paper mills in this country manufacture most of the pulp required
by them, viscose rayon plants depend entirely upon imports for their pulp
requirements. Specifications for viscose rayon grade pulp are more stringent
than for paper pulp and, therefore, manufacture of rayon pulp has not yet
been undertaken in India. Besides, coniferous woods which are usually used
for the manufacture of this grade of pulp are not available in sufficient
quantities at economic prices. In recent years, processes have been worked
out for the production of rayon pulp from hardwoods. Among these, the
water-prehydrolysis sulphate process has been found suitable for commercial
production. The *International Paper Company*, Natchez Division, Natchez,
(U.S.A.) are manufacturing rayon grade pulp from sweet gum (*Liquidambar
styraciflua*) by this process.

Blue gum (*Eucalyptus globulus* Labill) is being used for the manufacture
of viscose rayon pulp in Spain (Private communication from Urmeneta,
A.P.). Since 1956, *Eucalyptus saligna* Sm. is being used for the production
of rayon pulp by the bisulphite process in South Africa[1]. Investigations
carried out in Germany have indicated that viscose rayon grade pulp can
be prepared from sugarcane bagasse (from *Saccharum officinarum* Linn.)[2].
Costa *et al.*[3] have taken out a patent for the manufacture of dissolving pulp
from sugarcane bagasse.

Research work on the production of viscose rayon grade pulp from bamboo was started in this Institute early in 1951. Impetus to this line of research was given in 1954 by the suggestion from the Union Ministry of Commerce and Industry that priority should be given to research on the preparation of viscose rayon pulps from blue gum, wattle (*Acacia decurrens* Willd. and *A. mollissima* Willd.), etc. Of these, investigations carried out on the preparation of viscose rayon pulp from blue gum, using 20 per cent caustic soda (on oven-dry basis of pulp) for bleaching and refining processes have been published[4].

The results of investigations presented here relate to the following five cellulosic materials: (*i*) wattle (*A. decurrens* Willd.) ; (*ii*) blue gum ; (*iii*) *muli* bamboo (*Melocanna bambusoides* Trin.) ; (*iv*) *daba* bamboo (*Bambusa bambos* Vilm.) ; (*v*) sugarcane bagasse, adopting a multi-stage bleaching process and eliminating the refining process. The advantage of this process is that the consumption of caustic soda after digestion is only about 4 per cent. Pulps prepared from these sources have been found suitable for the preparation of viscose rayon on the basis of chemical purity. However, their suitability for viscose rayon manufacture can be confirmed only after the determination of their clogging constant in filterability test. This test will indicate the adjustments required in the various stages of manufacture of viscose, its spinning and subsequent processing. It has been proposed to send these samples abroad for evaluation of their clogging constant.

Blue gum billets received from Nilgiris, Madras State, were used. Debarked billets, 3 ft long × 7-10 in. diam. were chipped and the chips were screened. *Muli* bamboo (40 kg.), supplied by the Division Forest Officer, Cachar, Assam, was received in lengths of 6 ft, the diameter varying from 2 to 2.5 in.; the thickness of the wall was *c*. $\frac{1}{8}$ in. The bamboo was crushed and cut, and the pieces obtained were sieved.

Daba bamboo (two culms) was obtained from the Forest Research Institute demonstration area. The diameter of the culms was $1\frac{1}{2}$-2 in. and the thickness of wall, $\frac{1}{2}$-$\frac{3}{4}$ in. The bamboo was crushed and cut, and the pieces obtained were sieved.

Bagasse was received from the sugar mill at Doiwala (U.P.) some three years back. It had been stored under a roof without any covering on the sides. The bagasse was depithed according to the process described in an earlier publication. The depithed bagasse fibres, which amounted to about 65 per cent of the original bagasse, were used for pulping.

To prepare high alpha-cellulose pulps, the material was prehydrolysed with water under different conditions and then digested by the sulphate process. The liquor after water-prehydrolysis was examined for *p*H. The yield of

TABLE 1—WATER-PREHYDROLYSIS & SULPHATE DIGESTION OF CELLULOSE MATERIALS

	WATTLE	BLUE GUM	Muli BAMBOO	Daba BAMBOO	BAGASSE (DEPITHED)
Conditions of prehydrolysis					
(i) Material: liquor	1:4	1:4	1:4	1:4	1:6
(ii) Temperature, °C.	162	162	162	162	162
(iii) Time*, hr	3	2.5	4	4	3
(iv) pH of liquor after prehydrolysis	3.0	2.9	3.6	3.6	3.8
Conditions of sulphate digestion (NaOH:Na$_2$S=3:1)					
(i) Chemicals, %	18†	18†	22†	18†	16†
(ii) Material: liquor	1:3	1:3	1:4	1:4	1:6†
(iii) Temperature, °C.	153	153	162	162	170
(iv) Time*, hr	6	6	6	6	4
Alkali consumption, %	13.5†	15.6	19.5†	15.4†	14.8†
Yield of pulp (unbleached), %	37.1†	43.0†	32.2†	28.3†	34.7**

* This includes 1½ hr taken to raise the temperature to the final temperature.
† Expressed on oven-dry weight of original material.
‡ Expressed on oven-dry weight of prehydrolysed bagasse (depithed).
** Expressed on oven-dry bagasse (depithed).

TABLE 2—BLEACHING CONDITIONS OF PULP & YIELDS OF BLEACHED PULP

BLEACHING CONDITIONS	WATTLE	BLUE GUM	Muli BAMBOO	Daba BAMBOO	BAGASSE (DEPITHED)
First Stage					
(i) Chlorine water, %	1	0.5	1	1	2
(ii) Consistency, %	3	3	3	3	3
(iii) Temperature, °C.	20	20	23	22	24
(iv) Time, hr	1	1	1	1	1
Second Stage					
(i) Caustic soda, %	2	2	2	2	1
(ii) Consistency, %	5	5	5	5	5
(iii) Temperature, °C.	50	50	50	50	50
(iv) Time, hr	1	1	1	1	1
Third Stage					
(i) Sodium hypochlorite, %	2	2 1	1* 1	1* 1	1*
(ii) Consistency, %	5	5	3 5	3	3
(iii) Temperature, °C.	20	20	23	22	24
(iv) Time, hr	1	1	1	1	1
Fourth Stage					
(i) Caustic soda, %	2	2	2 1*	2	1
(ii) Consistency, %	5	5	5 3	5	5
(iii) Temperature, °C.	50	50	50 23	50	50
(iv) Time, hr	1	1	1	1	1
Fifth Stage					
(i) Sodium hypochlorite, %	1	1	1 2†	1	1
(ii) Consistency, %	5	5	5	5	6
(iii) Temperature, °C.	20	20	50	22	24
(iv) Time, hr	1	1	1	1	1
Sixth Stage					
(i) Sulphur dioxide, %	1‡	0.25	0.25 + 0.1* 1†	0.25 + 0.1*	0.25
(ii) Consistency, %	5	8	8 5	8	8
(iii) Temperature, °C.	20	20	23 50	22	24
(iv) Time, hr	1	1	1	1	0.5
Seventh Stage					
(i) Sulphur dioxide, %	0.25		0.25 + 0.1*	0.25 + 0.1*	
(ii) Consistency, %	8		8	8	
(iii) Temperature, °C.	20		23	23	
(iv) Time, hr	1		1	1	
Yield (on oven-dry material), %	35.6-35.8	41.2-41.5	29.7	25.3	30.7 (20 on whole bagasse)
Brightness (MgO taken as 100)	83	82	83-84	80-84	84

unbleached pulp was determined.   The pulp was bleached by a multi-stage bleaching process using chlorine, caustic soda extraction, sodium hypochlorite and sulphur dioxide.   In the bleaching process, the quantities of chemicals used, the sequence of treatment with different chemicals, etc., were varied. The yield of bleached pulp was determined.   The pulp was analysed for alpha-, beta- and gamma-celluloses, pentosans and ash according to the methods described earlier[1].   The brightness of the pulp was determined using a photoelectric reflection meter Model 610.

Conditions of water-prehydrolysis and sulphate digestion found suitable for yielding pulps of requisite chemical purity from the five cellulosic materials investigated and the yields of unbleached pulps are recorded in Table 1. Table 2 gives the bleaching conditions found suitable for these pulps, their yields and brightness.   Table 3 gives the results of chemical analysis of bleached pulps.

RESULTS AND DISCUSSION

Blue gum gave the highest yield (41.5%) of bleached pulp and bagasse, the lowest (20.0% on the weight of the original bagasse).   The yields of bleached pulp from *muli* bamboo and *daba* bamboo were 27.7 and 25.3 per cent respectively.   The brightness of the pulps was 80-84.   Previous work[1] has shown that the brightness can be increased to 88 by employing chlorine dioxide in the bleaching process.

The multi-stage bleaching process has helped to eliminate the refining treatment.   The sequence of treatment with different chemicals depends upon the raw material and the method employed for preparing the pulp.   The special multi-stage bleaching process seems to have been tried for the first time in this country.

The results recorded in Table 3 indicate that it is possible to prepare high alpha-cellulose pulps from wattle, blue gum, *muli* bamboo, *daba* bamboo

TABLE 3—CHEMICAL ANALYSIS OF BLEACHED PULPS

	WATTLE Av. %	BLUE GUM Av. %	*Muli* BAMBOO Av. %	*Daba* BAMBOO Av. %	BAGASSE (DEPITHED) %
Alpha-cellulose	96.40	94.95	93.00	97.05	95.5
Beta-cellulose	2.60	3.65	6.10	2.75	4.3
Gamma-cellulose	2.70	3.30	0.90	0.50	1.4
Pentosans	2.15	1.35	1.95	2.55	3.0
Ash	0.06	0.08	0.07	1.00	0.11

and sugarcane bagasse, and that they are suitable for the preparation of viscose rayon so far as chemical purity is concerned. A pulp of similar chemical purity prepared in an earlier investigation from blue gum using a refining process during bleaching has been found to have a satisfactory clogging constant in the viscose filterability test and, therefore, suitable for viscose rayon manufacture[5].

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Cellulose Ethers

C. D. DHARIYAL & V. B. CHIPALKATTI

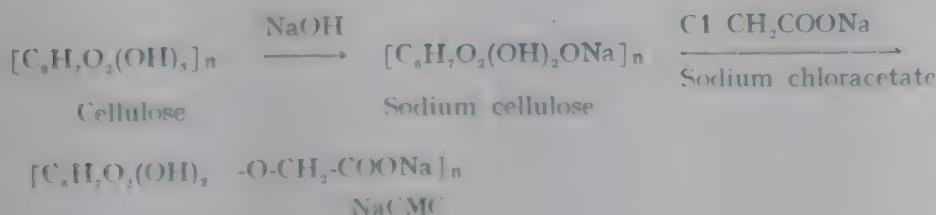Shri Ram Institute for Industrial Research, Delhi

The methods followed for the manufacture of sodium carboxymethyl cellulose (NaCMC), hydroxyethyl cellulose and ethyl cellulose are reviewed keeping in view their suitability to Indian conditions. The method of preparation of NaCMC by the slurry process using ethyl alcohol, developed by the Institute, is described. The properties of the product and economic aspects of manufacture are discussed.

Cellulose ethers such as carboxymethyl cellulose, hydroxyethyl cellulose, ethyl celluose have been known for a long time. They are characterized by their thickening, film forming and emulsion forming capacity and find extensive application in textile, paper, pharmaceutical, paint, lacquer and plastic industries[1-3]. Extensive investigations on these products have been carried out in U.S.A. and Germany.

Sodium carboxymethyl cellulose (NaCMC) and ethyl cellulose are imported into India. But the industry is unable to utilize them fully due to their high prices. However, the versatile nature of the compounds warrants intensive work and there are definite possibilities for increasing their consumption in the country.

The methods followed for the preparation of NaCMC, ethyl cellulose and hydroxyethyl cellulose are reviewed in this paper, and the results of investigations carried out under a scheme of research under way at the *Shri Ram Institute for Industrial Research*, Delhi, are summarized.

Sodium carboxymethyl cellulose (NaCMC)—The raw materials required for the manufacture of NaCMC are cellulose, caustic soda and chloroacetic acid. The reaction involved is:

$$[C_6H_7O_2(OH)_3]_n \xrightarrow{\text{NaOH}} [C_6H_7O_2(OH)_2ONa]_n \xrightarrow{\text{Cl CH}_2\text{COONa}}$$

$$\text{Cellulose} \qquad \text{Sodium cellulose} \qquad \text{Sodium chloracetate}$$

$$[C_6H_7O_2(OH)_2 \text{-O-CH}_2\text{-COONa}]_n$$

$$\text{NaCMC}$$

The processes employed by *Kalle & Co. A-G.*[5], Germany and *Wyandotte Chemicals Corporation*[6], U.S.A. were considered. They are unsuitable for adoption in India as the techniques and equipment are rather complicated and reaction control difficult. Besides, the products obtained by both processes are rather impure.

The process developed by the *Hercules Powder Co., U.S.A.*[7] has been examined in detail. In this process, *tert*-butyl alcohol or isopropyl alcohol is used as an inert medium for suspending cellulose. As it is uneconomical under Indian conditions to use these higher alcohols, ethyl alcohol which is cheap and easily available, was made use of as the suspending medium.

The methods used by *E. I. Dupont de Nemours & Co., U.S.A.*[8], *Imperial Chemical Industries Ltd.*[9], U.K., *Buckeye Cotton Oil Co., U.S.A.*[10], and *Uddeholm Aktiebolag*, Sweden[11], are also unsuitable as these involve steeping or shredding at one stage or another and a long reaction time (36-144 hr).

Hydroxyethyl cellulose

This is manufactured[12-14] by the action of ethylene chlorohydrin or ethylene oxide on sodium cellulose suspended in an inert medium of higher alcohol or hydrocarbon. The use of costly suspending medium rules out the possibility of adopting this process in India.

Ethyl cellulose—Of the different methods[15-17] described for the manufacture of ethyl cellulose, treatment of alkali cellulose with ethyl chloride in an autoclave at 175-400 lb./sq. in. at 150°C., appears to be the one which has proved economically successful. However, the consumption of ethyl chloride is high and the batch size is small. The use of a large autoclave would be uneconomical.

Diethyl sulphate is also used as an ethylating agent[18-21]. As its b.p. is higher than that of ethyl chloride, the reaction can be carried out at atmospheric pressure. However the quantity of diethyl sulphate used is abnormally high owing to the slow rate of reaction ; also it is rapidly hydrolysed under alkaline conditions.

WORK AT SHRI RAM INSTITUTE

Sodium carboxymethyl cellulose was chosen as the first product for investigation on account of the following considerations: (i) There is an immediate chance for its large consumption in the country (ii) the production of acetic acid in the country is expected to be stepped up as the manufacture of chloroacetic acid from acetic acid involves only one extra step.

It has been possible to develop a simple and elegant process of manufacture, using ethyl alcohol as the suspension medium.   It is reported that sodium carboxyethyl cellulose prepared according to the patented process of *Hercules Powder Co.*, in which ethyl alcohol is used as a slurrying medium, is unsatisfactory due to its low degree of substitution (D.S.) and hence insolubility in water.   However, investigations carried out at the *Shri Ram Institute for Industrial Research* have shown that it is possible to obtain a satisfactory and soluble product using ethyl alcohol.

Flow Chart 1 shows the method of manufacturing NaCMC using disintegrated cotton or purified linters as raw material.   The material is suspended in ethyl alcohol, mixed with the required quantity of caustic soda and simultaneously stirred in a jacketed vessel at 25-30°C.   Chloroacetic acid (solid) is then added gradually without allowing the temperature to rise above 35°C.   The whole mass is kept stirred and the temperature gradually raised to 50-55°C. during a period of one hr.   The stirring is continued for a further period of 1-5 hr depending on the requirement of D.S. and solubility.   The mass is then centrifuged to remove excess of alcohol, washed with alcohol and neutralized with acetic acid or solid sodium bicarbonate in alcohol suspension.   The centrifuged alcohol containing unreacted caustic soda can be reused for the next batch.   The mass is dried and ground for packing.   Initial laboratory trials were carried out with 25 g. of cellulose in a batch, and subsequently the batch size was stepped up to 1.5 lb. ; the yield fo final product was 3 lb.   A typical formula for the synthesis of NaCMC is : Cellulose, 1.5 lb. ; caustic soda, 2 lb. ; monochloroacetic acid, 2. lb. ; ethyl alcohol, 24 lb. ; and acetic acid, 150 g.

Table 1 gives the analysis of the laboratory product ; the analysis of 3 commercial samples are given for comparison.

TABLE 1—ANALYSIS OF NaCMC PRODUCED IN THE LABORATORY AND OF THREE COMMERCIAL SAMPLES

	MOISTURE %	NaCl %	NaCMC %	Na_2CO_3 %	$NaHCO_3$ %	GLYCOLATE ACETATE %	VISCOSITY cps.	D.S.
Shri Ram Institute	3.6	69	17.5	10	. .	. .	35	0.88
Hercules Powder Co.	4.5	90	3.6	. .	. .	1.8	25-20†	0.88
Samples from *Sardesai Bros.* Type—HS	8.0	46	18	6	2	28	25*	0.70
Type—B	7.0	56	20	2	10	14	10-20†	

* 1% solution.   † 2% solution.
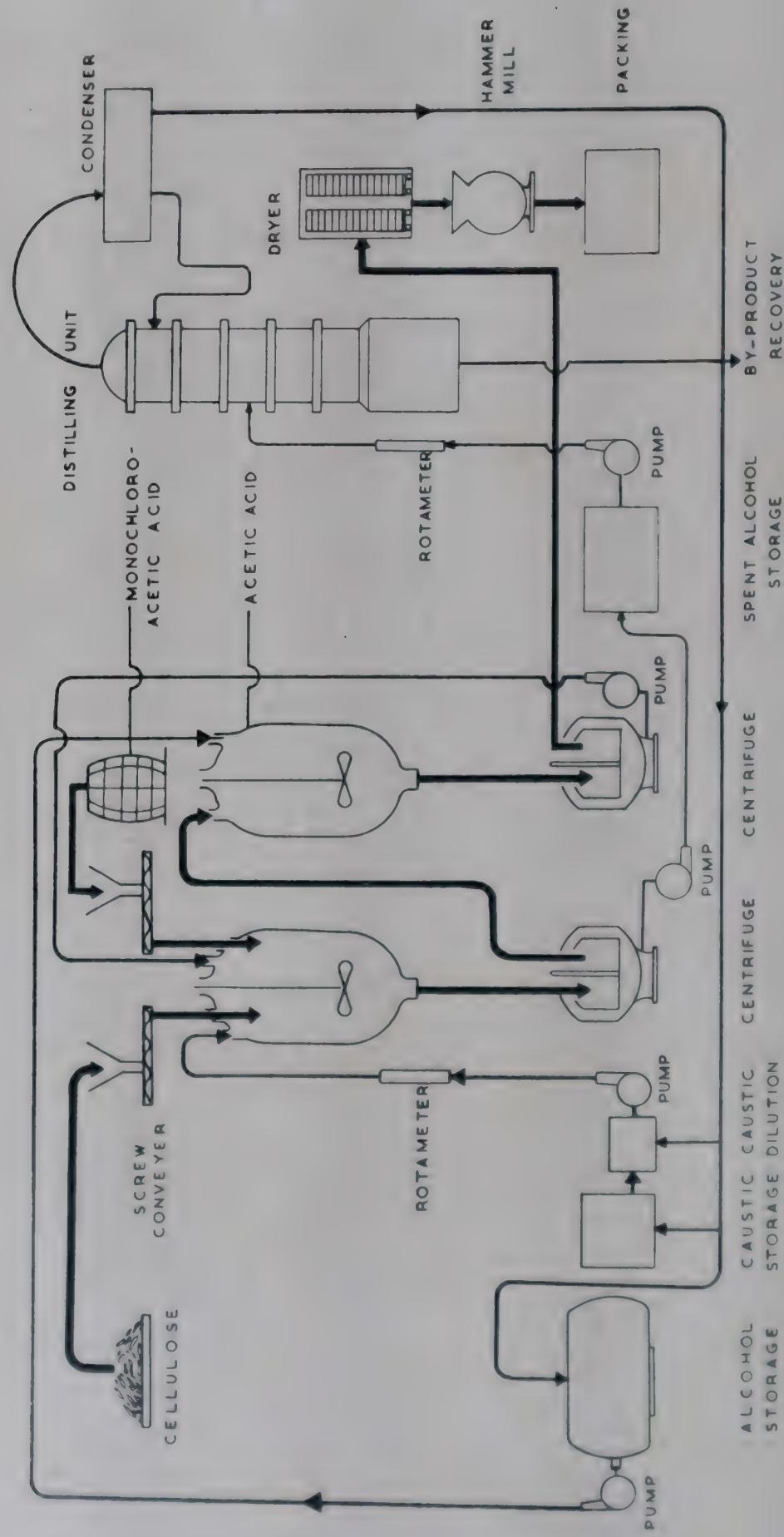
FLOW, CHART 1—MANUFACTURE OF SODIUM CARBOXYMETHYL CELLULOSE

The process developed at the Institute is simple. It requires a jacketed reaction vessel with a propeller type of stirrer. The final product can be ground in a hummer mill. It is now proposed to try this process on a pilot plant scale*.

The cost of manufacture of NaCMC has been found to be Rs. 2.45 per lb. (in spite of the high cost of chloroacetic acid) as against Rs. 3.50 per lb. of the imported product containing 60-70 per cent CMC.

Hydroxyethyl cellulose—A few trials with *tert*-butyl alcohol as the suspending medium and ethylene chlorohydrin as the hydroxy ethylating agent have been carried out and the product obtained has been found to be quite satisfactory. A typical formula for the synthesis of hydroxyethyl cellulose is: Cellulose, 40 g. ; caustic soda, 37 g. ; ethylene chlorohydrin, 24 g. ; *tert*-butyl alcohol, 1 kg. ; and sodium bicarbonate, 10 g.

Ethyl cellulose—Considerable work on the use of diethyl sulphate as alkylating agent has been carried out. So far, the results have not been proved satisfactory. A laboratory autoclave for treating one lb. of cellulose per batch has been designed.

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* Since presenting this paper, a pilot plant for making 100 lb. of NaCMC has been designed and put into commission.

Modern Trends in Pulp and Paper Manufacture

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So much advancement has taken place in recent years in the field of pulp and paper manufacture, and use of paper and board products that it is difficult to describe all the new developments in this review. An attempt is, however, made to deal briefly with trends in paper technology under three heads, viz. (i) fibrous raw materials, (ii) pulping processes, and (iii) paper manufacture.

FIBROUS RAW MATERIALS

A notable feature in the use of cellulosic raw materials for pulp and paper manufacture is the introduction of woods of the broad-leaved species (hardwoods) and sugarcane bagasse. Hardwoods are used for the manufacture of rayon pulp, grease-proof and glassine papers, tissue paper, newsprint and magazine paper, high class coated boards, corrugating medium, etc. There are several advantages in using hardwoods for pulp and paper manufacture. Writing and printing papers are being manufactured from sugarcane bagasse. Pine is being used for the production of newsprint.

PULPING PROCESSES

Several new pulping processes have been worked out and are being used on a commercial scale. Among them may be mentioned the continuous cooking process, mechano-chemical process, chemigroundwood process, cold caustic soda process, water-prehydrolysis process and the process of grinding and after-treatment of groundwood pulp from hardwoods with caustic soda to improve strength properties. Cooking of mixed woods is a new development. Multi-stage bleaching processes have been developed for manufacturing pulp of high brightness and for bleaching kraft pulps. The use of chlorine dioxide in bleaching is of comparatively recent origin. "Va purge" process is claimed to give more uniform and better pulps.

Paper Manufacture

New and more efficient equipment has been introduced in pulp mills for the removal of shives and grit from pulp and for chemical recovery. Instrumentation has become common in pulp mills in foreign countries.

In the manufacture of several varieties of paper, suitable refiners are being used to an increasing extent in the place of Hollander beaters and stock preparation is thus made continuous. Beater additives and "optical bleaching agents" are used to get the desired results. Some varieties of papers are manufactured from hitherto unused fibrous raw materials. Tissue and glassine papers and newsprint from hardwoods and newsprint from pine may be cited as examples. Kraft pulps are used to an increasing extent to replace sulphite pulp in newsprint manufacture.

To get more production, paper machines are being run at higher speeds. In some cases, wire width is also increased. Pick-up felts are used on high speed paper machines or on machines on which light weight papers are made. Two headboxes are used on the paper machine for handling two different kinds of stocks. Improvements have also been made in the design of flow box. More attention is being paid to heat recovery from the dryer section of paper machines. Specially designed equipment is used for detecting faults in paper during manufacture.

Mechanical Pulp from Hardwoods—
A Comparative Study

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Investigations carried out in India and elsewhere on the production of groundwood pulps from hardwoods have been reviewed and methods of improving their strength have been described.

Mechanical pulp is conventionally prepared by forcing under pressure a block of wood against a grindstone in the presence of water so that the wood is reduced to a fibrous condition, while the water keeps the stone cool, cleans and lubricates its surface and carries away the pulp. The term mechanical pulp includes pulps produced by other means, such as treating wood in log form with suitable chemicals under pressure and heat, and then grinding it, or treating wood chips with a solution of caustic soda at room temperature and fiberizing the softened chips in attrition mills. The pulp produced by the first process is known as chemigroundwood pulp and that produced by the second is known as cold caustic soda pulp.

The pulp used for the manufacture of newsprint and other printing papers should possess certain characteristics. Bulk, opacity, smooth surface and ability to receive sharp impressions of types and printing plates without blurring are important characteristics in newsprint. Besides, the cost of production of pulp on a large scale should be economical. These requirements are met from mechanical pulps obtained by wet grinding of suitable woods. It is cheaper to produce groundwood pulp because of its high yield and the comparatively simpler equipment employed in its manufacture. However, it is not possible to manufacture newsprint from 100 per cent mechanical pulp as it is not strong enough for the purpose. Generally 10 to 30 per cent chemical pulp is mixed with it to produce newsprint.

GROUNDWOOD PULPS

Groundwood pulps obtained from hardwoods are short-fibred, weak in strength properties, are of low brightness and, in many cases, highly colour-ed. Hence, production of newsprint from such pulps involves addition of

a higher proportion of costly chemical pulp and the use of a bleaching agent whose consumption is high.   Both these factors tend to increase the cost of production of newsprint.

Poplar wood was used for the production of pulp by the groundwood process when it was introduced for the first time.   Even now it is used for the same purpose but to a smaller extent.   Investigations on the use of spruce and other conifers revealed that these species have a number of advantages over poplar.   As the conifers were available easily and in abundance in regions where newsprint was manufactured, poplar fell into disuse.   The lack of know-how about handling hardwoods was also probably responsible for this.   However, as more and more knowledge was gained about the mechanism of grinding and as supplies of conifers began to dwindle, interest in the utilization of hardwoods for grinding purposes was revived.   A good deal of work has been done in this field in Europe, America and Australia. Mechanical pulps from eight varieties of American hardwoods (eastern cottonwood, yellow poplar, sugar maple, black tupelo, white ash, paper birch, sweet gum and quaking aspen) have been prepared and their strength properties and brightness have been determined[1,2].   Greenwood pulps from conifers (spruce) also have been prepared and their strength properties studied[3].   Screen analyses of mechanical pulps have also been carried out.

Investigations on the mechanical pulping of indigenous hardwoods have been carried out in India for the past few years.   Several hardwoods and some conifers have been investigated in the *Forest Research Institute*, Dehra Dun, with a view to finding out their suitability for the production of newsprint[4]. The potential availability of large quantities of short rotational wattle wood (*Acacia decurrens*) left after the extraction of tanning material from its bark and of the quick growing blue gum (*Eucalyptus globulus*)* have stimulated work in this field.   Trials on the mechanical pulping of these two woods have indicated that groundwood pulps with satisfactory strength properties can be produced from them[5].   *Sterculia campanulata* of the Andaman Islands and *Broussonetia papyrifera* (paper mulberry), a fast-growing broad-leaved species have been found to yield groundwood pulps with satisfactory strength properties[6,7].   Newsprint has been produced on a commercial scale in a paper mill using mechanical pulp from the latter species, and the paper has been given a printing trial on a high speed rotary press.

These investigations on Indian and American hardwoods show that when the hardwoods are pulped on a dull stone instead of a sharp stone, the consumption of energy is higher, production is lower and the strength properties better.   The strength properties of groundwood pulps from hardwoods are lower than those of spruce groundwood pulps.   The brightness of the American groundwood pulps is nearly the same as that of the Indian groundwood pulps.   Quaking aspen among American woods and

* Both species are used as fuel wood at present.

S. companulata among Indian woods yield groundwood pulps with high strength properties.

CHEMIGROUNDWOOD PULP

There are numerous references in literature since 1930 on the production of chemigroundwood pulps from pre-treated woods. Hytinnen and Schafer[1,8] at the *Forest Products Laboratory,* Madison (Wis.), U.S.A. have demonstrated that groundwood pulps produced from pretreated woods are stronger than those from untreated woods. The conditions of pretreatment were relatively milder than those followed later by Libby and O'Neil[9] at the *New York State College of Forestry*, Syracuse, New York. But due to the severe conditions of pretreatment, the groundwood pulps produced were much stronger. The commercial exploitation of the chemigroundwood process in America is the result of extensive research work carried out at Syracuse. The species of American hardwoods that have been investigated at these laboratories are paper birch, sweet gum, red alder, black tupelo, cottonwood, aspen, birch and beech. The wood is treated with solutions of sodium sulphite and sodium bicarbonate at a temperature of about 150°C. for a period of 6 hr. Vacuum and high hydraulic pressure up to 200 lb./sq. in. are employed for getting better penetration of liquors used for treatment. The strength properties are considerably improved, energy consumption is considerably decreased, freeness and longer fibre fraction are increased when groundwood pulps are prepared from pretreated woods. But the brightness of the pulps is low and pulps cannot be used without bleaching. However, it has been claimed by the Syracuse laboratory that the high cost of pretreatment of wood with chemicals and bleaching of resultant pulp is counterbalanced by the high strength properties of pulp and availability of hardwoods at a lower price in their region.

Chemigroundwood pulp is manufactured more successfully from hardwoods than from softwoods, since coniferous woods do not respond as favourably to this type of chemical treatment. Treated hardwood is ground with one-half to two-thirds power consumption and at double the production rate of spruce groundwood. The pulp itself is strong and is intermediate in this respect between spruce groundwood and unbleached sulphite pulp ; the chemigroundwood and unbleached sulphite pulp. The chemigroundwood process gives yields of 85-90 per cent on the weight of original wood. Most species of hardwoods yield chemigroundwood pulps which may be bleached with peroxide or calcium hypochlorite to the same final brightness as spruce pulp and at no greater cost. Research work on the pulping of blue gum by the chemigroundwood process has recently been started at the *Forest Research Institute*, Dehra Dun, and the results obtained are encouraging.

Caustic soda treatment of groundwood pulps

Another method of improving the strength properties of groundwood pulps

is to treat them with a solution of caustic soda at 50°C. for a period of 2-3 hr. The pulp is then washed free of dissolved matter and used for paper making.

Neale et al.[10] found that strength properties of Eucalypt groundwood pulp increase on treatment with caustic soda. Foote and Parsons[11] observed improvement in strength properties of aspen groundwood pulp by this treatment. Bhat and Virmani[12] have also shown in the case of blue gum that caustic soda treatment of groundwood pulp improves the strength properties. These investigations have further revealed that strength properties increase with the temperature of treatment, whereas freeness, yield and brightness of pulps are lowered. The pulps can, however, be brightened by partial bleaching with a mixture of sodium peroxide and hydrogen peroxide.

CONCLUSION

A comparison of the strength properties of groundwood pulps, chemiground-wood pulps and groundwood pulps treated with caustic soda shows that woods of broad-leaved species cannot be ruled out for the manufacture of mechanical pulps. Some hardwoods yield groundwood pulps with satisfactory strength properties and they can be used as such for the manufacture of newsprint. The woods, however, should be of light shade as the brightness of pulp depends upon the colour of wood used. In the case of a majority of woods, groundwood pulps are of interior quality. In such cases, the chemi-groundwood process or caustic treatment of groundwood pulp can be advantageously employed. These treatments improve the strength properties considerably and in many cases these pulps obtained are superior to ordinary groundwood pulps from conifers. This development is of considerable importance to countries like India, where conifers are not available easily at economic prices and woods of broad-leaved species may become available in large quantities in the near future.

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Cold Caustic Soda Pulps and Writing and Printing Papers from Wattle Woods

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Laboratory scale experiments on the cold caustic soda pulping of two species of wattle wood, *Acacia decurrens* and *A. mollissima*, separately and mixed in equal quantities by weight and two pilot plant trials for the production of writing and printing papers from wood chips of the two species are described.

The cold caustic soda process of pulping was developed recently at the *Forest Products Laboratory*, Madison, Wisconsin, U.S.A. It was first used for making pulp for corrugated boards ; more recently it has been used on a commercial scale at *Gould Paper Mill*, Lyons Falls, N.Y., U.S.A., for making pulp from a mixture of birch, beech, maple and other available hardwoods. In 1957, 35 tons of this pulp per day were produced and used in admixture with other suitable pulps for making printing paper. The advantages of the cold caustic soda pulping process have been described in an earlier publication[1].

The barks of two species of wattle, *Acacia decurrens* (green wattle) and *Acacia mollissima* (black wattle) are used in the tanning industry. These two exotic species are now grown in Nilgiris and Upper Palni hills of Madras State. Plantings on a large scale were started some years back and it is expected that in due course of time, 30,000 tons of wattle wood would be available per year in Upper Palnis and another 12,000 tons per year in Nilgiris. It is understood that these plantations are being extended.

After the removal of the bark for use in tanning, the wood should be available at a cheap price for pulp and paper manufacture. Hence, investigations[2-4] were undertaken by the author and his associates at this Institute for studying the suitability of wattle wood for the manufacture of writing and printing papers. The results of the investigations are described in this paper.

TABLE 1—CONDITIONS OF COLD CAUSTIC SODA PULPING & YIELD OF PULP

(Material : Liquor = 1 : 4. Period of Caustic Soda Treatment‡, 4 hr)

	CONCN OF CAUSTIC LIQUOR g./l.	TOTAL CAUSTIC SODA* %	TEMP. OF LIQUOR °C.	CONSUMPTION OF CAUSTIC SODA* %	PERIOD OF KOLLER-GANGING min.	UNBLEACHED PULP YIELD* %	BLEACH CONSUMP-TION† %	BLEACHED PULP YIELD* %
A. decurrens	25	10	32	6.0	20	88.8	2.9	86.3
	50	20	33	7.9	15	85.3	2.9	82.5
	75	30	31	10.3	10	83.2	2.9	79.7
A. mollissima	25	10	31	5.8	20	77.7	2.9	76.5
	50	20	31	7.4	15	...	2.9	76.7
	75	30	31	8.8	10	76.7	2.9	74.4
A. decurrens + A. mollissima (50 : 50)	25	10	31	6.1	20	83.2	2.9	80.6
	50	20	31	8.4	15	82.9	2.9	80.5
	75	30	31	9.3	10	80.3	2.9	79.2

* On basis of oven-dry raw material.

As available chlorine on basis of oven-dry unbleached pulp

Raw Materials

A. decurrens and *A. mollissima* supplied by the Range Officer, Coonoor, Madras State, were used for laboratory and pilot plant trials. The debarked billets were 3 ft long × 1.5-10 in. diam. They were chipped separately in a chipper and screened on the two-deck vibratory screen (Waterous Make).

A number of laboratory experiments were carried out using wood chips of each of these species separately and also mixed together in equal quantities.

Experimental Procedure

For each experiment, 150 g. chips (oven-dry basis) were soaked in caustic soda solutions (600 ml.) containing 25, 50 and 75 g. of caustic soda per litre for a period of 4 hr at room temperature (31°-33°C.) under atmospheric pressure. Excess liquor was decanted off and the chips were washed twice with water equal in volume to the quantity decanted which was about 400 ml. Washed chips were passed through the Sprout-Waldron Refiner at 8 per cent consistency using successively 1.016 mm., 0.381 mm., 0.381 mm., 0.127 mm., 0.127 mm., and 0.127 mm. clearance between the two discs of the Refiner. The pulp was washed on a 66-mesh sieve and worked in the kollergang at 8 per cent consistency (on the basis of oven-dry original chips). The time of kollerganging varied from 20 to 10 min. depending on the state of the refined pulp. After washing the pulp on a 66-mesh sieve, the yield of unbleached pulp was determined. The freeness of the pulp was about 650 ml. (C.S.F.).

A portion of the pulp was partially bleached with bleaching powder equivalent to 2.9 per cent available chlorine (on the basis of oven-dry pulp) at room temperature (31° to 33°C.) at about pH 9. The yield of bleached pulp was determined.

Unbleached and partially bleached pulps were beaten separately in the Lampen Mill and standard sheets were made. Strength properties were determined after conditioning the sheets at 65 per cent relative humidity (R.H.) and 26°C. The brightness of standard sheets made from unbleached and bleached pulps was measured by means of the photoelectric reflection meter (Photovolt Corporation, U.S.A. Model 610) and the results were expressed on the basis of the brightness of magnesium oxide – 100.

Details of experimental conditions, yields of unbleached and partially bleached pulps and bleach added are given in Table 1. Strength properties and brightness of standard unbleached pulp sheets are given in Table 2 ; the corresponding data for bleached pulp sheets are recorded in Table 3.

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TABLE 2.—STRENGTH PROPERTIES OF UNBLEACHED PULP SHEETS (CONDITIONED AT 65% R.H. & 26 C.)

	Freeness of pulp ml. (C.S.F.)	Basis weight g./sq.m.	Breaking length (Schopper) m.	Stretch %	Tear factor (Marx-Elmendorf)	Burst factor (Mullen)	Folding endurance (Schopper) double folds	Brightness %
A. decurrens	305	62.0	3020	2.3	61.8	21.0	27	38
	276	60.0	3170	2.6	68.7	24.4	33	35
	300	60.0	2860	2.5	63.8	22.0	20	37
A. mollissima	309	59.6	2390	1.9	46.1	14.3	6	35
	304	63.6	2320	2.3	48.8	16.5	7	32
	304	62.8	2180	2.1	49.1	18.4	7	32
A. decurrens + f. mollissima (50:50)	270	60.8	2800	2.4	56.7	18.9	22	37
	294	59.6	2790	2.3	59.2	19.2	14	36
	275	60.8	2230	2.3	59.2	20.8	14	34

TABLE 3.—STRENGTH PROPERTIES OF BLEACHED PULP SHEETS (CONDITIONED AT 65% R.H. & 26°C.)

	FREENESS OF PULP ml. (C.S.F.)	BASIS WEIGHT g./sq.m.	BREAKING LENGTH (Schopper) m.	STRETCH %	TEAR FACTOR (Marx-Elmendorf)	BURST FACTOR (Mullen)	FOLDING ENDURANCE (Schopper) double folds	BRIGHT-NESS %
A. decurrens	310	60.8	3050	2.5	64.2	23.5	28	47
	279	62.0	3130	2.8	66.1	23.7	30	43
	278	59.6	3110	2.4	68.5	24.1	23	45
A. mollissima	276	60.8	2520	2.0	50.4	17.1	10	43
	300	61.6	2390	2.3	52.4	16.9	10	45
	314	60.6	2410	2.2	55.8	20.3	10	43
A. decurrens + A. mollissima (50 : 50)	326	62.0	3010	2.5	57.3	19.7	24	46
	278	60.0	3110	2.7	62.0	21.8	22	43
	278	60.0	2810	2.6	64.5	24.3	24	45

TABLE 4—COLD CAUSTIC SODA PULPING OF A. DECURRENS **&** A. MOLLISSIMA

	TRIAL No. 1	TRIAL No. 2
Concn of caustic soda liquor, g./1.	50	50
Total caustic liquor*,%	20	20
Temp. of liquor, °C.	35	31
Period of treatment, hr	4	4
Consumption of liquor, %*	7.0	7.7
Unbleached pulp yield, %*	85.2	87.1
Bleach consumption, %†	2.86	3.11
Bleached pulp yield, %*	78.8	77.0

* Expressed on basis of oven-dry material.
† As available chlorine expressed on basis of oven-dry screened unbleached pulp.

PILOT PLANT TRIALS

In order to confirm the suitability of wattle wood for the production of cheap grade writing and printing papers, two pilot plant scale trials were carried out. In each case, chips of the two species were mixed in equal proportions by weight for caustic soda treatment. About 430 lb. chips (on oven-dry basis) containing 14.8 per cent moisture were used in the first trial and about 420 lb. chips (oven-dry basis) containing 12 per cent moisture in the second trial. The treatment was carried out in a vertical stationary mild steel digester of forced circulation type (c. 3 cu.m. capacity) at atmospheric pressure for a period of 4 hr. Caustic soda liquor (50 g./1.) containing 20 per cent caustic soda on the weight of chips (on oven-dry basis) was circulated at room temperature. The initial temperatures of caustic soda liquor in the two cases were 35°C. and 31°C. respectively. The temperature of the liquor had risen during circulation by 11°C. in the first trial and by 7°C. in the second. After treatment, the spent liquor was pumped into a storage tank and the chips washed twice in the digester with cold water equal in volume to the spent liquor collected.

Treated chips were fiberized in a rod mill containing 34 rods of different diameters and having a total weight of about 545 kg. The pulp was then kollerganged for 15 min. and washed in a potcher. The unbleached pulp was partially bleached with bleaching powder equivalent to 2.0 per cent of available chlorine in the first trial and 3.1 per cent available chlorine in the second. Table 4 gives the conditions for caustic soda treatment, bleach consumption and pulp yields.

The bleached pulp was beaten in the factory Hollander beater and mixed with 20 per cent bamboo sulphate pulp (bleached and beaten) prepared by cooking bamboo chips with 24 per cent total chemicals (NaOH:Na₂S = 3:1).

TABLE 5—STRENGTH PROPERTIES OF STANDARD PULP SHEETS FROM BLEACHED AND BEATEN BAMBOO SULPHATE PULP (CONDITIONED AT 65% R.H. & 26°C.)

Freeness, ml. (C.S.F.)	256
Basis weight, g./sq. m.	56.0
Breaking length, m.	4050
Stretch, %	4.3
Tear factor	178
Burst factor	33.0
Folding endurance, double folds	330

TABLE 6—STRENGTH PROPERTIES OF PAPERS FROM PULPS (CONDITIONED AT 65% R.H. & 26°C.)

	TRIAL 1*	TRIAL 2*
Freeness after size addition, ml. (C.S.F.)	335	300
Ream weight, 17½ in. × 22½ in.—500, lb.	15.9	17.2
Basis weight, g./sq. m.	50.7	57.0
Thickness, microns	103	109
Tensile strength (Schopper) for 1 cm. width, kg.		
Machine direction	1.45	1.49
Cross direction	0.69	0.70
Breaking length†, m.		
Machine direction	2860	2610
Cross direction	1360	1230
Stretch, %		
Machine direction	1.4	2 6
Cross direction	2.6	2 0
Tearing resistance, g.		
Machine direction	30	41
Cross direction	32	42
Tear factor†		
Machine direction	59.2	71 9
Cross direction	63 1	73 7
Bursting strength (Mullen), kg./sq. cm	0 60	0 53
Burst factor†	11 8	9 3
Folding endurance (Schopper), double folds		
Machine direction	6	5
Cross direction	3	3
Brightness, %	47	51

* Correspond to those in Table 4
† On the basis of oven-dry weight of paper

at 153 C. for a total period of 6 hr. The pulp was washed and bleached with bleaching powder in the potcher and beaten in the factory beater. Dry sheets of bamboo pulp made on the paper machine were used for admixture with cold caustic soda pulps in the two experiments. Strength properties of standard sheets made from bamboo pulp sheets are given in Table 5.

Rosin size, 3.0 per cent and alum, 9.0 per cent were added to the mixture of beaten wattle wood and bamboo pulps in each of the two trials. No loading agent was added in the first ; in the second trial, however, 9.4 per cent china clay was added. Writing paper was made in the first trial on the Fourdrinier paper machine and printing paper was made in the second. The Fourdrinier machine was run at its maximum speed of 15 m. per min. The running of paper was satisfactory. Since wattle wood is short-fibred, bamboo pulp was used in the furnish.

Data on the strength properties and brightness of writing and printing papers made on the pilot plant are recorded in Table 6.

DISCUSSION AND CONCLUSION

The results given in Table 1 indicate that with increase in the concentration of caustic soda liquor there is an increase in the consumption of caustic soda by chips of A. decurrens and A. mollissima and also by the chip mixture. In all cases, the yields of unbleached and bleached pulps generally decrease with increase in the concentration of caustic soda liquor ; the decrease in pulp yields is, however, appreciable in the case of A. decurrens. There is no appreciable loss during the partial bleaching of pulps with bleaching powder. A. decurrens gives higher yields of pulps than A. mollissima.

It is clear from the results recorded in Table 2 that there is no appreciable change in the breaking length of pulp sheets from both species of wood when the concentration of caustic soda liquor is increased from 25 to 50 g./l. There is, however, a decrease in the breaking length when the concentration of caustic soda liquor is further increased to 75 g./l. In the case of A. decurrens pulp, tear factor, burst factor and folding endurance increase when the concentration of caustic soda liquor is increased from 25 to 50 g./l. but they decrease in value when the concentration is further increased to 75 g./l. In the case of A. mollissima, there is generally an increase in the values of these three properties when the concentration of caustic soda liquor is increased from 25 to 75 g./l. The brightness of pulps from these two species is only slightly affected when the concentration of caustic soda liquor is increased from 25 to 75 g./l.

Both species give satisfactory pulps by this process. Pulps from A. decurrens are, however, better than those from A. mollissima.

A comparison of the strength properties of groundwood pulps from *A. decurrens* given in an earlier publication[4] with those of cold caustic soda pulps given in Table 2 shows that the latter pulps are stronger than the former.

On comparing the results given in Table 2 with those given in Table 3, it is evident that there is no appreciable change in the strength properties of unbleached and bleached pulps and that the brightness considerably improves by partial bleaching with bleaching powder.

The results recorded in Tables 1-3 indicate that both species on treatment with caustic soda solution (50 g./l.) for a period of 4 hr give pulps in high yields ; the pulps appear to be suitable for the manufacture of writing and printing papers.

The results of pilot plant trials given in Tables 4 & 5 confirm that pulps are obtained in high yields from a mixture of *A. decurrens* and *A. mollissima* by the cold caustic soda process and that the pulps can be used for making cheap quality writing and printing papers with satisfactory strength properties. Since these hardwoods are short-fibred, a long-fibred pulp such as bamboo pulp will have to be mixed with the pulps in suitable proportions for producing paper on commercial machines which are run at high speeds.

The economics of the cold caustic soda process depend largely on the recovery of caustic soda. One of the ways of recovering the chemical is to add spent caustic liquor to a large volume of caustic soda of the strength used for treatment and draw the liquor for the next treatment from the storage. By this method, the strength of the storage solution falls down only after some cycles. When this occurs, the storage solution is made up to the required strength by the addition of fresh caustic soda. Experience has shown that this method works satisfactorily.

It should be possible for the mills in South India to use *A. decurrens* and *A. mollissima* for the production of cheap grade writing and printing papers using the cold caustic soda process.

ACKNOWLEDGMENT

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Anatomical Features of Bamboo Used for Paper Manufacture

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Anatomical structures of *Dendrocalamus strictus* Nees and *Bambusa arundinacea* Willd. used for paper making have been studied in detail. Variations in cellular constituents from bottom to top and from periphery to centre of culm are described with particular reference to fibres.

Besides conifers and hardwoods, bamboo, among grasses, forms one of the chief raw materials for the production of pulp. The fibres along with parenchyma constitute the two tissues of bamboo used. Bamboos are fundamentally different from both hardwoods and softwoods in their mode of growth and tissue organization ; the tissues are formed exclusively from primary growth while in hardwoods and conifers, the tissues originate mainly from secondary growth. Due to this basic difference, the different tissues of bamboo are longitudinally aligned whereas in hardwoods and softwoods they are arranged both vertically and radially. Another striking difference is in the distribution of parenchyma cells. In woods, the fibrous tissues form the main bulk in which parenchyma and ray cells are dispersed in complicated patterns. In bamboo, on the other hand, parenchyma cells form the ground mass in which the fibro-vascular tissues are characteristically arranged. Further, as a result of primary growth, a basic uniformity in tissue organization is maintained throughout the length of the bamboo culm. The component tissues, mainly fibres and parenchyma, however, vary at different levels of the culm in shape, size, and wall thickness, which are traceable to differences in growth and maturity. These variations also appear to have some bearing on their quality and suitability for paper making. Some of the salient anatomical characteristics of different tissues are, therefore, discussed here.

Growth of bamboo culm

Bamboo is unique from the point of view of its growth. The full length of the culm is attained during a short period of 3-4 months. The culm is cylindrical in shape : maximum in girth at the bottom and gradually

decreases towards the top. The culm is divided into several internodes separated by nodes. As a rule, the longest internodes are found near about the middle of the culm. It will be shown later that these internodes are characterized by longest elements. As the rate of growth slows down, it results in the gradual decrease in the length of the internodes towards the top of the culm.

In order to understand the process and course of maturation of the culm and the nature of the constituent elements, a short account of the growth phenomenon in bamboo will not be out of place here. The young shoots as they come out of the ground during the growth season represent a full culm in its miniature form. The internodes are formed in acropetal succession. The elongation of all the internodes is due to the activity of the intercalary meristem situated at the base of each internode and takes place successively starting from the bottom towards the top of the culm. As each internode starting from the bottom reaches full length, it ceases its activity while the rest continues to elongate. This goes on for all the internodes till the full length has been attained. Secondary thickening in cell wall becomes conspicuous only when the full length has been attained. This takes place first in the lowest internode and progresses successively in other internodes in acropetal order.

Structural topography of internode

The tissue organization in bamboo exhibits the typical anatomical structure of grasses. The internode consists of two types of tissues, namely prosenchymatous and parenchymatous. The former is composed of elongated thick-walled fibres arranged in close association with vessels and phloem elements, forming long continuous fibro-vascular strands running vertically. The latter constitutes the thin-walled ground mass in which the fibro-vascular bundles are arranged. The orientation of all the cells is in the vertical direction. Ray tissue with characteristic radial arrangement as found in woods is conspicuous by its absence (Pl. 1, Fig. 3).

In the fibro-vascular bundles occurring in the inner portion of the internode, the fibres are arranged in four distinct masses or caps (Pl. 1, Fig. 1c). Of these, three are associated with xylem elements and one with the phloem. Of the former, two are laterally placed on either side of the large metaxylem vessels, while the third subtends the crushed protoxylem vessel (Fig. 1). Towards the periphery all three xylem caps tend to fuse together to form a single large mass. As a result, vascular bundles occurring in the periphery have typically two caps instead of four as in the centre (Pl. 1, Fig. 1a).

The peripheral bundles are, as a rule, small, numerous and crowded forming a compact zone. Towards the inside of the bamboo, the size of fibrovascular bundles along with constituent elements gradually
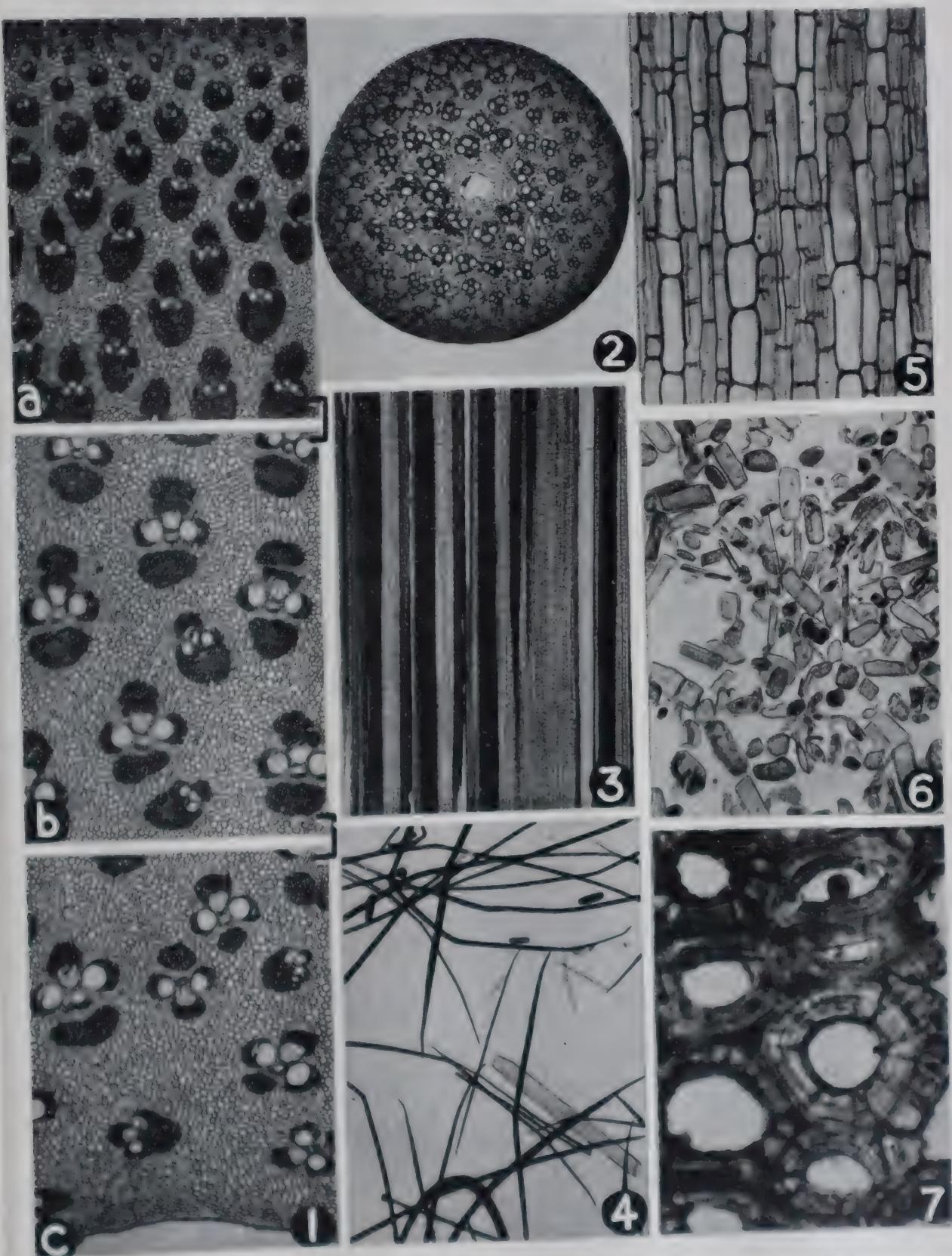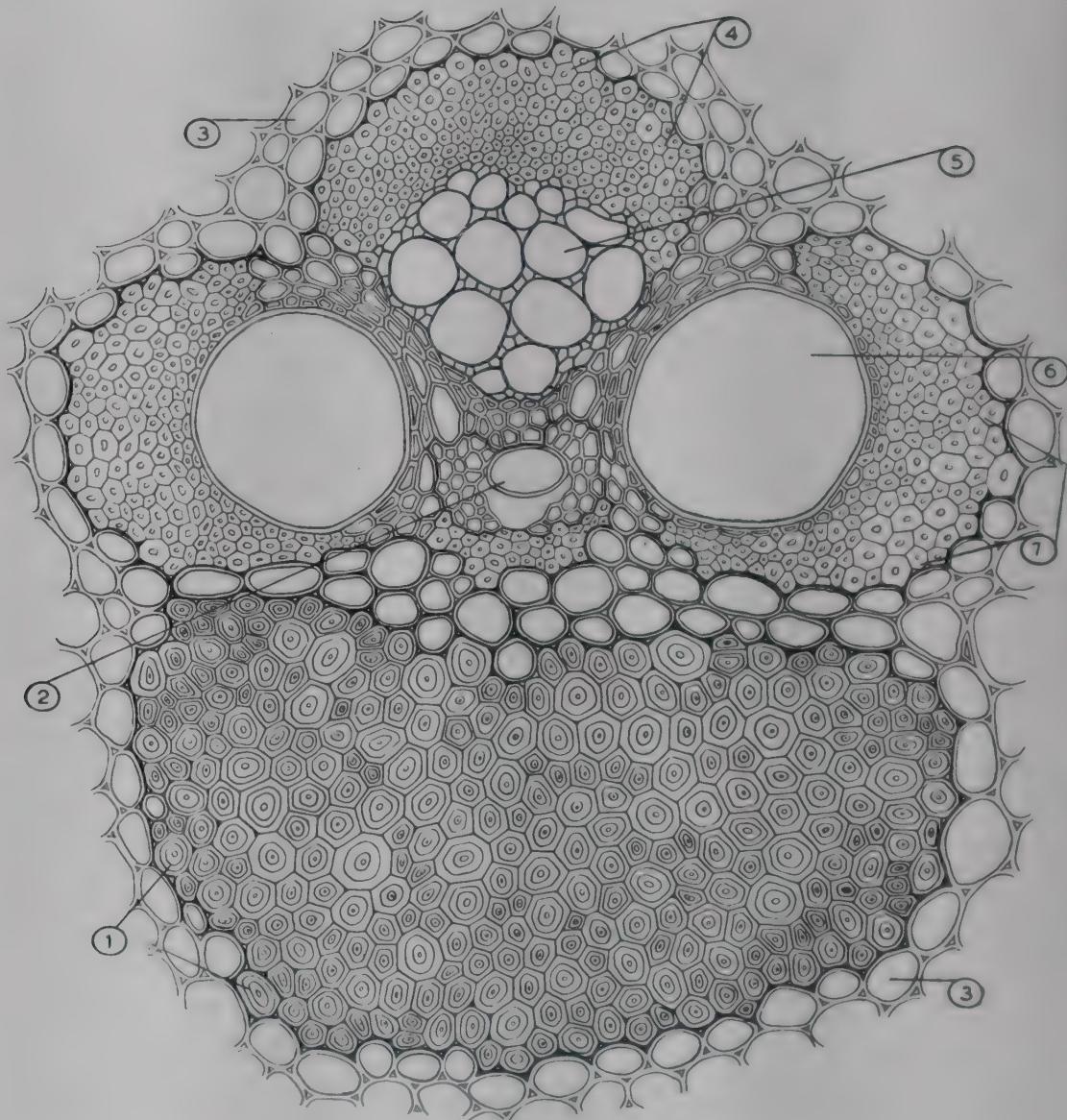
PLATE 1

Fig. 1—Anatomical details of a vascular bundle of *Dendrocalamus strictus* Nees (× 360) [(1) Median xylem fibre cap, (2) Protoxylem, (3) Parenchyma, (4) Phloem fibre cap, (5) Phloem, (6) Vessel and (7) Metaxylem fibre cap]

increases (Pl. 1, Fig. 1a,b). At the same time these bundles become more widely spaced with abundance of ground tissue in between. The phloem, which forms a characteristic tissue of the bundles, consists of sieve tubes and companion cells (Fig. 1). The cortical zone may be almost absent as in *D. strictus* (Pl. 2, Fig. 11) while it may be very distinct as in *B. arundinacea* (Pl. 2, Fig. 10). The largest number of fibro-vascular bundles occurs in the lower internodes of the culm and shows a gradual decrease towards the top. This is due to the fact that a number of them pass into the leaf and branch at each node.

Structure of node—Nodes are a prominent feature in all grasses. In annual grasses and cereal straws, however, they are small and not so hard and,
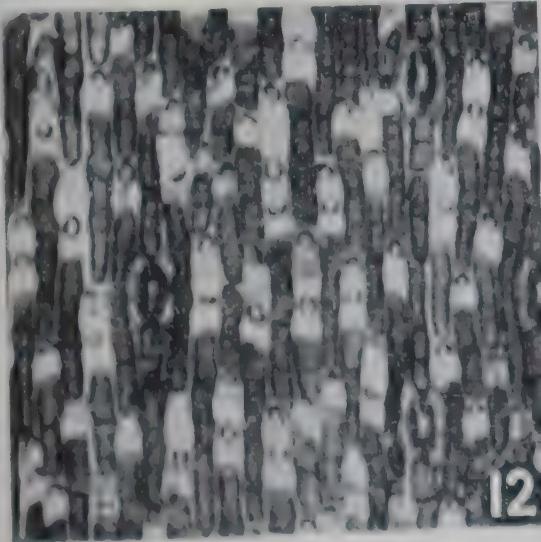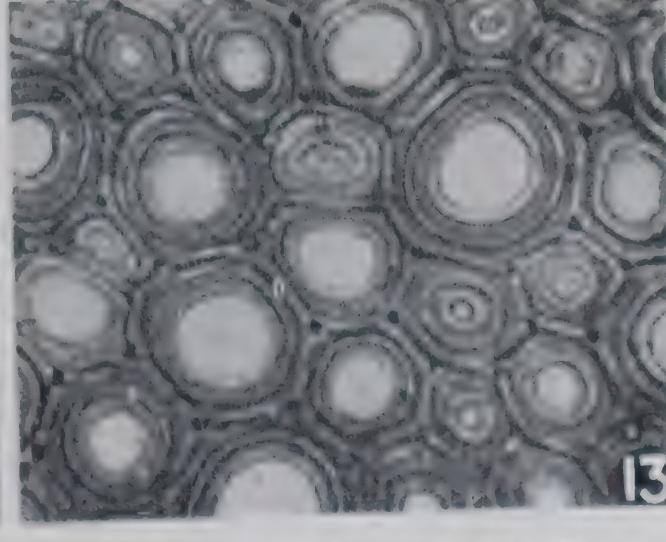
PLATE 2
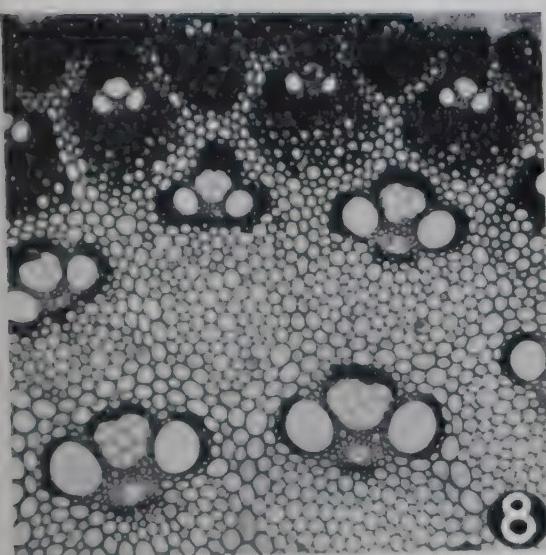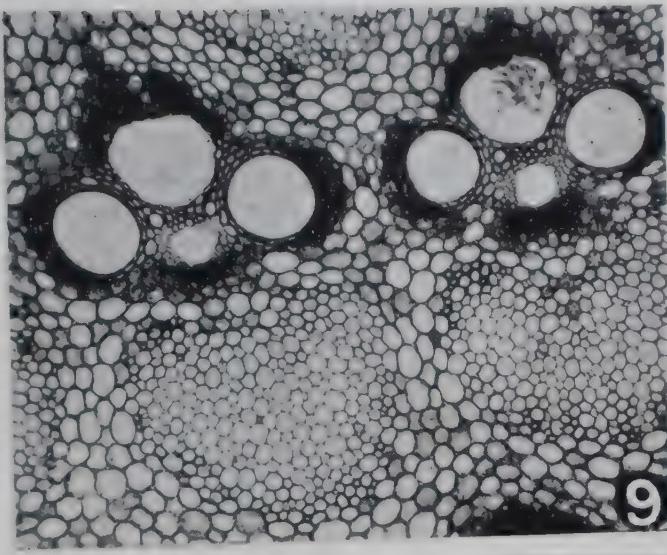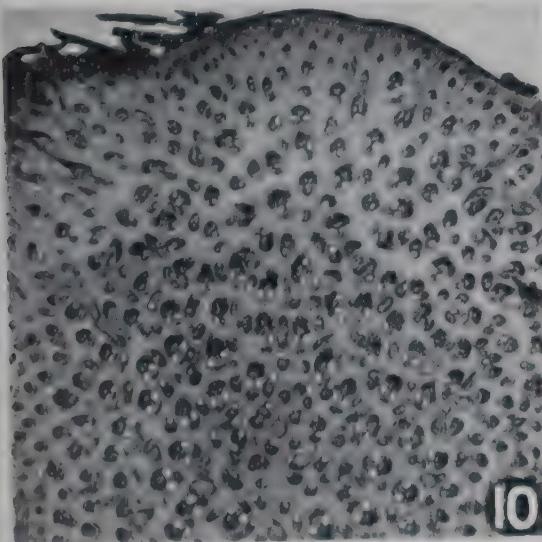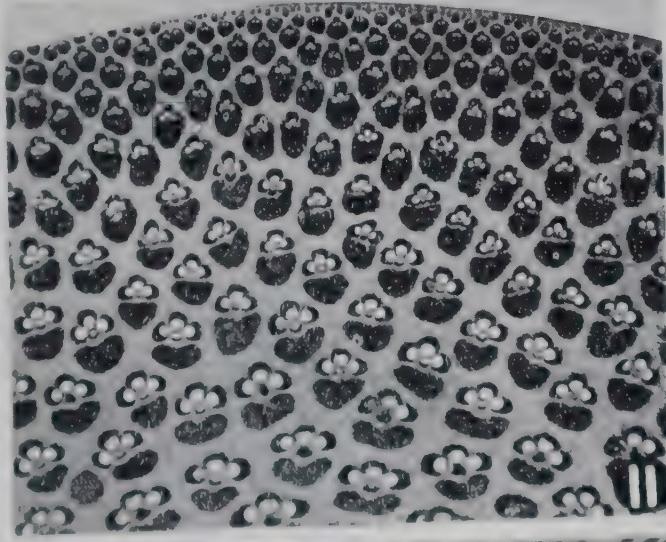
FIG. 8-13. *Dendrocalamus strictus* NEES. 8—CROSS-SECTION SHOWING PERIPHERAL BUNDLES (×63); 9—CROSS-SECTION OF A YEAR OLD CULM (×63) (NOTE TWO IMMATURE FIBRE CAPS); *Bambusa arundinacea* WILLD.; 10—CROSS-SECTION SHOWING COMPLEX STRUCTURE OF NODE (×7); 11—CROSS-SECTION FROM MIDDLE OF THE CULM SHOWING MATURE FIBRES (×10); 12—STEM EPIDERMIS SHOWING LONG AND SHORT CELLS WITH SILICA (×260); 13—CROSS-SECTION SHOWING STRATIFIED FIBRE WALLS (×630)

therefore, give little difficulty to the paper maker in digesting the material. On the other hand, in bamboo, the nodes are large, hard and comparatively more lignified. In structure, the nodes are more complex than the internodes as regards the course of vascular strends. Throughout the length of an internode the bundles take a fairly straight and vertical course. At the node most of them pass almost straight or with a slight bend to the other contiguous internodes, while some of them anastomese with the leaf bundles as well as with the bundles of axillary buds forming a complicated pattern. As regards the distribution of fibres in the node, the phloem fibre cap has been found to be comparatively larger in size than the xylem fibre cap, and in this respect it is just the reverse of what we see in the internodes (Pl. 2, Fig. 10).

Distribution of fibres—It has been reported that the fibres constitute about 60-70 per cent of the weight of bamboo. Therefore, their distribution as well as anatomical, physical and chemical properties are bound to have considerable effect on the yield and quality of paper. The fibre content is far in excess of the parenchyma in the peripheral portion while towards the inside, parenchyma predominates (Pl. 1, Fig. 1a,b,c). Vertically the fibre distribution is the highest in the internodes situated at $\frac{1}{4}$ to $\frac{1}{2}$ heights of the culm which also contains the longest and the highly matured fibres (Pl. 2, Fig. 11). From this part onwards, up to the extreme top, though the proportion of fibres is greater than in the parenchyma, the nature of fibres is not the same (Pl. 1, Fig. 2). Towards the top of the culm, the fibres show a gradual decrease in their length and degree of maturation (Pl. 2, Fig. 8). Towards the bottom of the culm the proportion of fibres is greater in the outer one-third portion (Pl. 1, Fig. 1a) of the internodes while in the inner two-third (Pl. 1, Fig. 1b,c), the proportion of parenchyma is greater than the fibres, as the fibro-vascular bundles are wide apart and much less in number than in the periphery (Pl. 1, Fig. 1a,b,c).

In the peripheral fibro-vascular bundle with two distinct caps, the xylem fibre cap is comparatively large in size than the phloem fibre cap (Fig. 2). Towards the inside also, the median xylem fibre cap is the largest in size. Next is the phloem fibre cap, while the lateral metaxylem fibre caps are the smallest (Pl. 1, Fig. 1c). The size of the metaxylem fibre caps gradually decreases towards the top. In the top one-third portion of the culm, the relative sizes of various caps are difficult to make out due to insufficient lignification (Pl. 2, Fig. 8,9).

Shape, size and length of fibres—Bamboo fibres show considerable variation in shape, size and wall-thickness. They are usually long and straight with pointed and gradually tapering ends (Pl. 1, Fig. 4). The wall may be thin to very thick with corresponding decrease in the lumen. The length of the
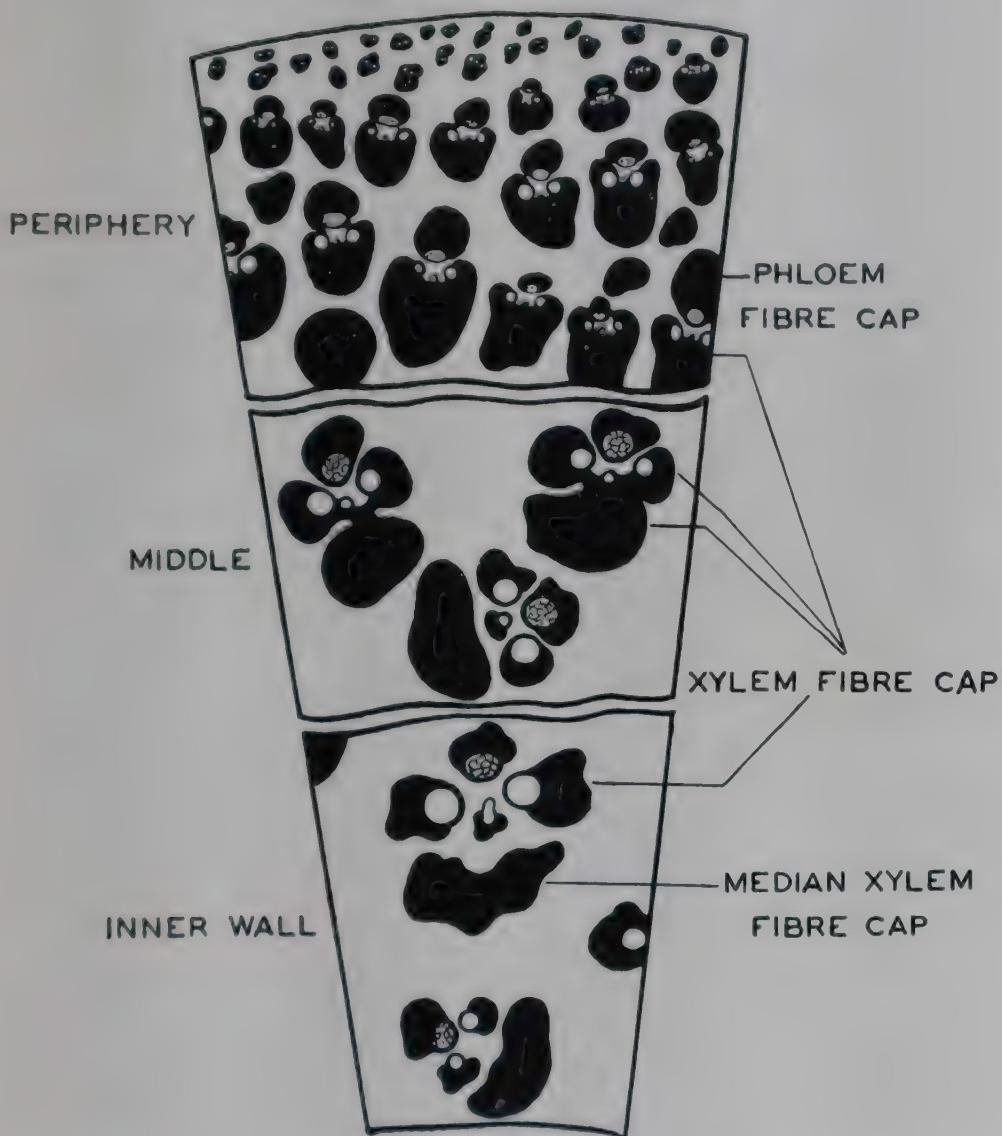
FIG. 2—DIAGRAMMATIC TRANSVERSE SECTION OF AN INTERNODE OF *Dendrocalamus strictus* NEES (IN PART) FROM PERIPHERRY TO THE INNER WALL (× 30)

fibres varies from 0.31 to 5.18 mm. and diameter, from 3.5 to 52.5µ. The average length of the fibre is about hundred times the diameter.

Observations made on fibre length at different heights of the culm have shown that the length is correlated with the length of internodes (Fig. 3). The longest fibres are found in the middle region of the culm where the internodes are longest. Towards the bottom and top, the internodes are comparatively short with corresponding decrease in fibre length (Table 1).

The fibre length varies also in different caps at any one level from the periphery inwards. Towards the inside, the mean fibre length of the median xylem cap is significantly longer than that of either metaxylem or phloem caps. Again, the mean length of metaxylem cap fibres is longer than that of phloem cap fibres (Table 2). Similarly, in peripheral bundles, it has been

found that the mean fibre length of xylem cap fibres is significantly longer than that of the phloem caps (Table 3).

The diameter of the fibres on the other hand, varies in a somewhat different manner. It is found to be large in the extreme bottom internodes, showing a gradual fall up to $\frac{1}{4}$ height of the culm. After this height, the fibre diameter is again seen to rise attaining its maximum and remaining more or less constant up to the middle or so of the culm beyond which there is again a gradual fall to the extreme top.

Septate fibres—Septa resembling those of hardwoods have been observed in fibres of both *D. strictus* and *B. arundinacea*, particularly in culms which have attained an age of one year or more. This indicates that the formation of septa in bamboo fibres occurs when the culm has attained its full length. As regards their frequency the maximum number is found to occur in the median xylem fibre caps, followed by metaxylem and phloem fibre caps (Fig. 2).
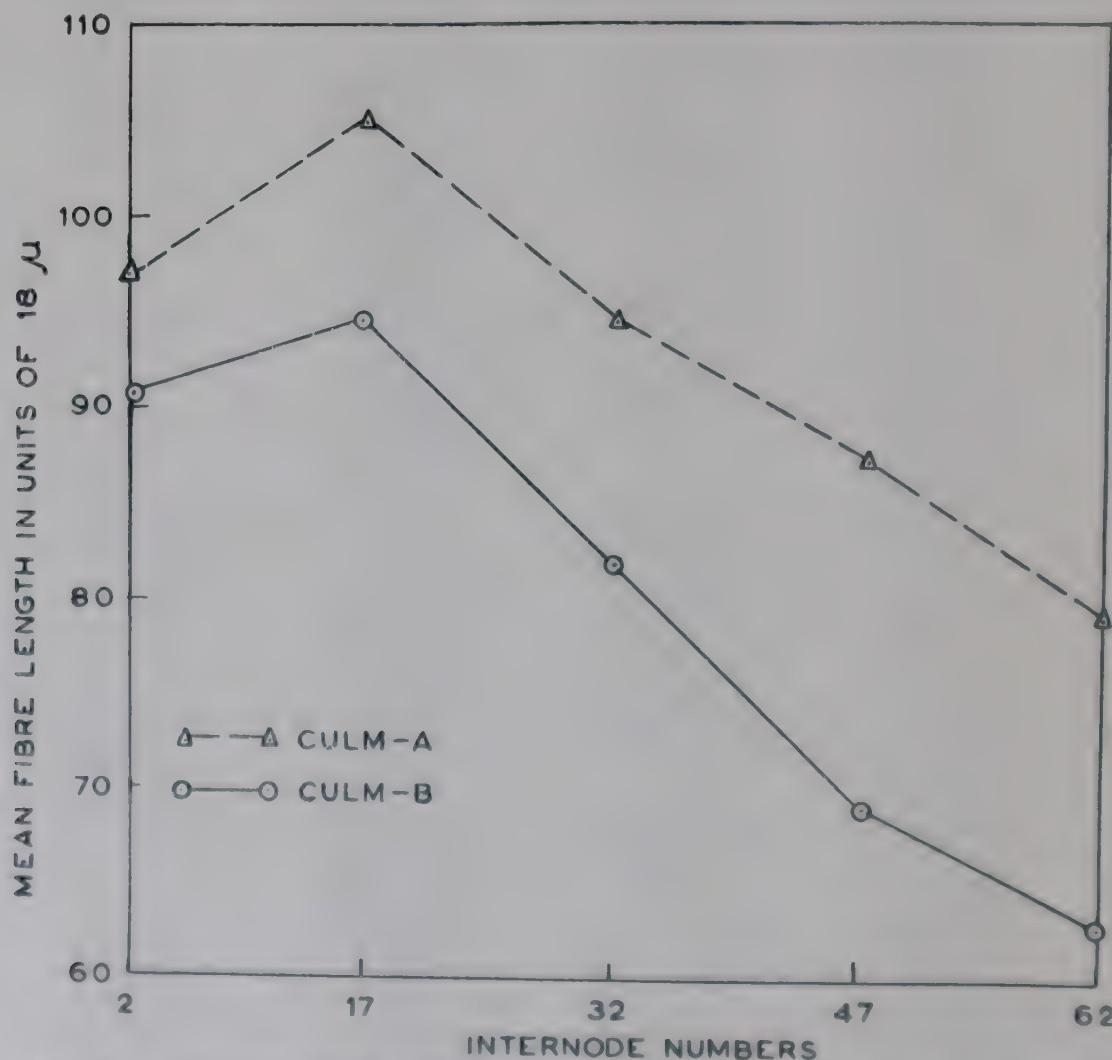

Fig. 3—Mean fibre length versus internode numbers of *Bambusa arundinacea*

TABLE 1—MEAN FIBRE LENGTH AT DIFFERENT HEIGHTS IN BAMBUSA ARUNDINACEA

INTERNODE No.	LENGTH OF INTERNODE *in.*	FIBRE LENGTH* μ
2	3.0	272 - 1,846 (634)
17	12.3	308 - 3,946 (1,629)
32	11.0	326 - 3,149 (1,358)
47	10.0	344 - 2,697 (1,086)
62	7.0	308 - 2,172 (923)

* Figures in brackets relate to mean value.

TABLE 2—MEAN FIBRE LENGTH IN DIFFERENT CAPS OF VASCULAR BUNDLES IN THE MIDDLE PORTION OF THE WALL

FIBRE	INTERNODE 2 MEAN FIBRE LENGTH		INTERNODE 12 MEAN FIBRE LENGTH		INTERNODE 26 MEAN FIBRE LENGTH	
	Dendro-calamus μ	*Bambusa* μ	*Dendro-calamus* μ	*Bambusa* μ	*Dendro-calamus* μ	*Bambusa* μ
Outer group, phloem fibre cap	1,000	1,582	1,910	1,812	1,633	1,654
Lateral groups, meta-xylem fibre cap	1,321	1,962	2,305	2,042	2,076	1,835
Inner group, xylem fibre cap	1,402	2,628	2,502	2,715	2,410	2,281

TABLE 3—MEAN FIBRE LENGTH IN DIFFERENT CAPS OF PERIPHERAL VASCULAR BUNDLES

FIBRE	INTERNODE 2 MEAN FIBRE LENGTH		INTERNODE 12 MEAN FIBRE LENGTH		INTERNODE 26 MEAN FIBRE LENGTH	
	Dendro-calamus μ	*Bambusa* μ	*Dendro-calamus* μ	*Bambusa* μ	*Dendro-calamus* μ	*Bambusa* μ
Outer group, phloem fibre cap	1,280	1,864	1,891	1,893	1,968	1,564
Inner group, xylem fibre cap	1,365	1,966	2,162	2,056	2,209	1,853

Structure and distribution of parenchyma—The parenchyma tissue is much more abundant in bamboo than in hardwoods. The proportion of parenchyma appears to be the highest in the bottom internodes gradually decreasing towards the top. Similarly, it is found to be very much reduced near the epidermis and shows a marked increase towards the inside. The parenchyma cells collectively form into loosely joined ground tissue extending throughout the width of the internode, through which fibro-vascular bundles are scattered. The parenchyma cells are nearly isodiametric in cross-section and usually have their long axis vertical. They are thin-walled and very

small in size and are of two distinct types. The predominant type is usually greater in length than in width (56-154μ in length and 28-58μ in width), comparatively thick-walled and lignified. The other type is very short, 14-28μ in height, more or less rectangular, squarish or roundish in shape and appears to have thin unlignified walls. The latter, on account of their minute size, are of little importance from the point of view of paper making (Pl. 1, Fig. 5,6). The parenchyma cells do not show much variation in their dimensions at different heights of the culm, the only difference being in cell wall thickening and lignification. The lignification as shown by staining reactions is feeble at the top gradually becoming strong towards the base of the culm. In older culm, towards the periphery as well as the inside of the middle internodes, the parenchyma cells may often become heavily sclerosed. The sclerosed cells, on account of their thick lignified walls and reduced lumen, may offer some difficulty in pulping (Pl. 1, Fig. 7).

Skin of epidermis—The epidermis is the outermost single layer of rectangular cells and is covered externally by a thick waxy cuticle. It displays a uniform pattern being composed of two distinct types of cells—one long and the other extremely short. A short cell may either be a cork cell (suberised) or a cell containing silica. These are always found in pairs and are arranged alternately with the long cells in distinct longitudinal rows (Pl. 2, Fig. 12). The pattern is striking and affords an easy method of separating the two species discussed here. Because of its high silica content the removal of epidermis may be desirable.

Maturation of tissues—It has already been mentioned that the full length of bamboo is attained within a short period of 3-4 months. The fibres at this stage are thin-walled and are composed mainly of cellulose. When the full length of the fibre is attained, the secondary thickening of the cell wall becomes noticeable followed by lignification. The secondary wall of the fibre is very thick and shows distinct stratification (Pl. 2, Fig. 13). The progress of secondary thickening as well as lignification throughout the length of the culm is from bottom to top. It is important to note that though the general trend of fibre maturation is from bottom to top, the maximum secondary wall thickening and lignification in fibres appear to be in the region of $\frac{1}{4}$ to $\frac{1}{2}$ height of the culm (Pl. 2, Fig. 11). In the top internodes, the secondary thickening and lignification are noticeable only in the peripheral bundles, while in the inner bundles, the fibres show hardly any secondary thickening and lignification, particularly in the large median xylem caps (Pl. 2, Figs. 8,9). The process of cell wall thickening and lignification practically cease after 2-3 years so that even in mature bamboos, the top portion remains poorly lignified. In view of this as well as of the relatively smaller dimension of the cell constituents in the top, bamboo cuttings from the top are likely to yield a different grade of cellulose and pulp than the bottom and middle portions.

Refining of Indian Cotton Linters.   G. S. Sidhu, S. Zainulabideen & Iqbal Ahmed (Regional Research Laboratory, Hyderabad).

Laboratory experiments on the refining of Indian cotton linters obtained from a delinting mill in Hyderabad and from a delinting plant in the laboratory, to chemical cotton (alpha-cellulose, 99%) are described.

The linters were purified by digestion with sodium hydroxide solution of different concentrations under varing pressure and time.   Souring of digested linters to reduce the ash content, de-ironing and bleaching were also studied under different conditions to obtain chemical cotton suited for nitration to cellulose nitrate of explosive and lacquer grades.   (*Abstract*)

Microscopical Studies on Degradation of Jute Fibre by Microorganisms

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The object of the investigation is to make a direct visual study of how fungal and bacterial growth starts and proceeds on the jute fibre. Cotton is the only vegetable fibre in which investigations on these aspects have been carried out using staining techniques or a combination of staining and swelling techniques. Cotton, however, differs in many fundamental respects from jute. It is easier to observe internal growth in cotton without any swelling pretreatment as it is unicellular fibre ; the lumen would perhaps be more easily penetrated by fungal hyphae as one end of the fibre is open. In bast fibres, the pectinous and other materials present in the middle lamella may have an effect on the progress of microbiological growth. Besides, the chemical composition of the fibre being different from that of the cotton fibre, the extent as well as the nature of microbiological growth may be expected to be different. Modified or new method are therefore necessary for studying the microbiological degradation of jute.

Methods of study

Since it was essential for the purpose of this study to have suitable methods for the detection of fungal and bacterial growth on and in the fibre, attention was first directed to the development of such methods. Differential stains used on cotton for detecting fungal growth include Victoria Blue B preceded by swelling in cuprammonium solution (Prindle[1]), methyl violet preceded by swelling with caustic soda (Hall and Elting[2]), and basic fuchsin followed by aqueous phenol (Rogers et al.[3]). Very recently Rose et al.[4] carried out a comparative study of various staining agents and selected Pianese IIIb (Martius Yellow S + malachite green + acid fuchsin) as the most satisfactory stain, hyphae and fibre being coloured red and green respectively. The test is however laborious and delicate in operation.

Bacterial growth on cotton has been recently studied by Heyn using Winogradsky's original technique : staining by acid erythrosin followed by

aqueous gentian violet showed up the organisms as pink against a colourless background.

All the tests mentioned above were applied to mildewed jute fibre.   None gave satisfactory differential staining.   Cotton Blue and other stains were absorbed by the fibre as well as by hyphae, and were therefore unsatisfactory for the detection of surface growth.   However, a stain has been independently discovered (2.5% Chlorazol Sky Blue), which stains the hyphae leaving the fibre colourless.

For the study of internal growth it was found essential to loosen the ultimate cells to some extent before staining.   Swelling in 10 per cent sodium hydroxide solution, followed by application of pressure on the cover slip with a slight circular motion, has been found to be the best technique for this purpose.   Where necessary, the alkali was washed out before the application of stain.   Here again, none of the stains tried by other workers proved entirely satisfactory.   Pianese IIIB, however, did show up the hyphae as red within the lumen, but also gave rise to artefacts due to local accumulation of stain along the uneven surface of the fibre*.   Since this test also required careful timing of the different steps, extent of washing, etc. in order to obtain consistent results, it was temporarily abandoned in favour of Chlorazol Sky Blue and Carwright's stain, which gave satisfactory results. The latter stain (a mixture of safranin and picroaniline) colours the hyphae deep blue and the ultimate cells light violet.   It has been used on woody tissues but not on textile fibres.   However, it has to be borne in mind that even ordinary fresh bast fibres sometimes show thread-like materials in the lumen area when swollen.

Side by side with the observation of microbiological growth on or in the fibre, tests were performed to estimate the extent of damage caused.   Loss in tensile strength and loss in weight were determined using jute fabric and fibre respectively.   In addition, the damage count (based on a microscopical test") was determined.   Jute fibres were incubated in contact with a mineral salt solution and fabric strips were incubated in a saturated atmosphere.

RESULTS

Experiments with a mixture of 5 typical jute-decomposing fungi showed the appearance of hyphal growth within the lumen of incubated fibres in 3 days The extent of such growth increased with increase in incubation period and corresponding increase in damage.

When inoculated individually, however, only 3 of the 5 species showed

* Rose et al. from insufficient experience with jute claim these to represent fungal hyphae

penetration into the lumen within 6 days. The point or mode of entry has not yet been clearly detected. Five other species, not considered as jute-decomposers, did not show penetration. In every case, there was appreciable hyphal growth, often accompanied with sporulation, on the fibre surface. Damage count and loss in weight showed some increase.

Both external and internal gorwth appeared later in fabrics than in fibres, and in unsterilized fibres than in sterilized fibres, under the experimental conditions.

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Microbial Decomposition of Cellulose with Special Reference to Cotton and Cotton Fabrics

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A knowledge of the mechanism of microbial degradation of cellulose is essential for the solution of problems not only in textile technology but also in various other fields, such as agronomy, biochemistry, paper and wood technology and disposal of sewage.

Losses due to microbial attack in the textile industry in U.S.A. have been assessed at about $1 billion a year[1] although great care is taken in the country to prevent destruction of cotton and cotton fabrics. The extent of losses incurred in India is not known. An idea regarding the alarming magnitude of damage can be had from the report of the *Technical Development Establishment Laboratories*[2,3], Kanpur, that British ordnance installations in India wrote off stores annually worth Rs. 12.5 millions between 1944 and 1947 and about Rs. 1 million in the second quarter of 1947.

Neither a survey of causes of damage to cotton and cotton fabrics nor a study of causative microorganisms and their mode of action on cellulose has been carried out in India. It is only in the light of these investigations, proper measures could be taken to prevent the collosal loss during the storage of cotton under Indian conditions.

The claim that the microbial picture may be considerably different in Indian conditions is borne out by the fact that although the microbiological flora of air and soil are nearly the same in different parts of the world, there are important specific differences. For instance, the cellulolytic fungus *Memnoniella echinata* is the dominant species attacking cotton fabric throughout South Pacific areas. This organism has been isolated rarely from similarly exposed fabrics in Panama[4].

Investigations on microbial and biochemical changes involved during the process of retting of Kenaf (*Hibricus sabdarifa* Linn.) and Malachra (*Malachra capitata* Linn.) have revealed that organisms belonging to the genus *Pseudomonas* are dominant in the process of retting and decomposition of pectin. These observations are of considerable value since available information from the work of European and Australian investigators pointed only to organisms of the genus *Clostridium* as chiefly involved in the process of retting. *Pseudomonas* are non-spore formers, Gram-negative and highly aerobic, while *Clostridia* are spore-bearing, Gram-positive, and anaerobic in character. Likewise it is expected that microflora responsible for the destruction of cotton and textile fabrics in India may be different from the one pictured from the results reported abroad.

It is also of interest to note that apart from the cellulolytic microflora which are distributed universally, there are those which are exclusive to the soil, destroying fibres coming in contact with it, those which metabolize exclusively on finishes and bring about secondary damage to fibres, and those which are confined to sea water and disintegrate the fibres in sea water alone.

A review of literature reveals that with the exception of the work by Basu[4] on fungal decomposition of jute fibre and a few stray papers on protective measures recommended to prevent mildew attack, no published data on cellulolytic microorganisms destroying cotton and cotton fabrics in India are available.

Considerable attention has been paid in U.S.A. to investigations on cellulolytic fungi. Marsh and Bollenbacher[5] observed that angiocarpous forms like *Leptosphaeria*, *Diplodia*, *Diplodiella*, etc. are of common occurrence in prolonged sunny exposures, whereas *Alternaria* and *Cladosporium* are common only in the early stages ; *Aspergillus*, *Pencillium*, *Memnoniella*, etc. which are not common in the above situations are dominant in humid and shaded exposures only. The reports of White *et al.*[8] and Pady *et al.*[9] show that there is little evidence to show that similar cellulolytic fungi are geographically distributed all over the world. Buston and Basu[10], Mandels and Norton[11], Darby and Goddar[12], and recently Whitaker[13], have gathered valuable information on the physiology and biochemistry of some cellulolytic moulds, such as *Chaetomium globosum* and *Myrothesium verrucaria*.

Greathouse[14], Abrams[15], Dean *et al.*[16], and Siu[1] have mainly contributed to our knowledge in this field. Of these investigations, Siu reports that much of the work on microbiological damage to cotton and cotton fabrics has been confined to cellulolytic fungi, and less effort has been expended on the isolation of bacteria which are equally devastating to cotton fabrics. Heyn[17] has recently carried out some work on bacterial degradation of cotton.

In the microbial deterioration of cellulose, specific adaptive enzymes are secreted, which split the polysaccharide into water soluble compounds which get diffused are further metabolized. The presence of two enzymes, one capable of coverting cellulose to a water soluble compound and the other of hydrolysing it further to glucose, is widely accepted. However, it has not been demonstrated conclusively that the action of cellulose stops at the cellobiose stage. Further, no efforts have been made so far, to isolate the breakdown products other than glucose and cellobiose ; the enzymes involved in the crystalline form are yet to be isolated.

Although considerable amount of work has been done abroad on the biochemical mechanism of cellulose decomposition, the fundamental problem regarding the exact pathway in the hydrolysis of cellulose remains unanswered. Data and theories presented by various investigators on the subject are contradictory.

For carrying out these studies, microbially damaged samples may be collected from godowns of textile mills in India. Taxonomic studies of various microbial entities involved will have to be undertaken employing suitable techniques for isolation and identification of causative microorganisms. Observations on the characteristic structures of organisms *in situ* and pure culture studies on the mode of action as well as on the nutritional requirements of dominant isolation should also be carried out.

ACKNOWLEDGMENT

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